PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :
C07D 239/34, 239/38, 239/42, 239/46, 239/52, 239/56, 403/06

A2

(11) International Publication Number: **WO 00/49001**

(43) International Publication Date: 24 August 2000 (24.08.00)

(21) International Application Number: PCT/US00/03180

(22) International Filing Date: 8 February 2000 (08.02.00)

(30) Priority Data:
60/120,130 16 February 1999 (16.02.99) US
60/139,302 15 June 1999 (15.06.99) US

(71) Applicant *(for all designated States except US)*: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and

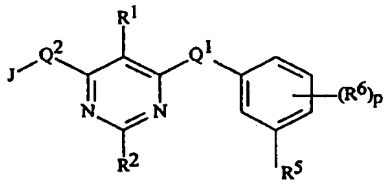
(75) Inventor/Applicant *(for US only)*: STEVENSON, Thomas, Martin [US/US]; 103 Iroquois Court, Newark, DE 19702 (US).

(74) Agent: BIRCH, Linda, D.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19808 (US).

(81) Designated States: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: PHENOXYPYRIMIDINE INSECTICIDES AND ACARICIDES



(I)

(57) Abstract

Compounds of Formula (I), and their *N*–oxides and agriculturally suitable salts, are disclosed which are useful as arthropodicides wherein Q^1 is O, S, NR^{17}, $OCR^{18}R^{19}$, or $NR^{17}CR^{18}R^{19}$; wherein when Q^1 is $OCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$, then Q^1 is attached to the pyrimidine through the O or N atom respectively; Q^2 is S, CR^3R^4, $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$; wherein when Q^2 is $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$ then Q^2 is attached to the pyrimidine through the O, S or N atom respectively; R^1 and R^2 are each independently H, C_1–C_4 alkyl, halogen, NR^7R^8, C_1–C_4 alkoxy, C_1–C_4 haloalkyl, C_1–C_4 alkylthio or nitro; each R^5 is independently H, halogen, C_1–C_4 alkyl, C_1–C_4 haloalkoxy, C_1–C_4 haloalkyl, C_1–C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11}; each R^6 and each R^{22} is independently H, halogen, cyano, C_1–C_4 alkyl, C_1–C_4 haloalkyl, C_1–C_4 haloalkoxy, C_1–C_4 alkoxy, NR^{17} or $S(O)_nR^9$; p is 0–4; and J, R^3, R^4R^7, R^8, R^9, R^{11}, R^{17}, R^{18}, R^{19} and n are as defined in the disclosure. Also disclosed are compositions containing the compounds of Formula (I) and a method for controlling arthropods which involves contacting the arthropods or their environment with an effective amount of a compound of Formula (I).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

TITLE

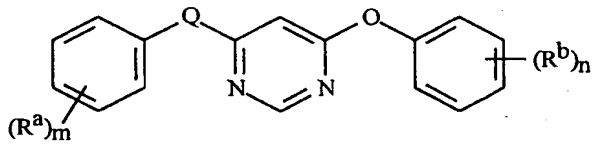
PHENOXYPYRIMIDINE INSECTICIDES AND ACARICIDES

BACKGROUND OF THE INVENTION

This invention relates to certain phenoxypyrimidines, their *N*-oxides, agriculturally suitable salts and compositions, and methods of their use as arthropodicides in both agronomic and nonagronomic environments.

The control of arthropod pests is extremely important in achieving high crop efficiency. Arthropod damage to growing and stored agronomic crops can cause significant reduction in productivity and thereby result in increased costs to the consumer. The control of arthropod pests in forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health is also important. Many products are commercially available for these purposes, but the need continues for new compounds which are more effective, less costly, less toxic, environmentally safer or have different modes of action.

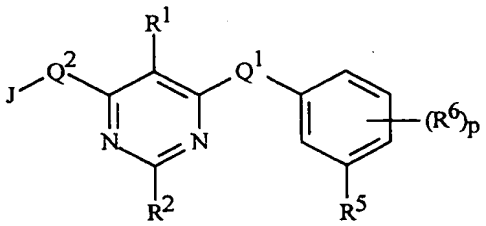
4,6-Diphenoxypyrimidines (Q is O in the formula below) are disclosed in US Patent 5,707,995 as insecticides and acaricides. 4-Anilino-6-phenoxypyrimidines (Q is NH in the formula below) are disclosed (WO 98/12184 and WO 98/54154) as insecticides and acaricides. JP99/269154 discloses phenoxypyrimidines wherein Q in the formula below can be certain nitrogen-containing groups.



The phenoxypyrimidines of the present invention are not disclosed in these publications.

SUMMARY OF THE INVENTION

This invention is directed to compounds of Formula I, including all geometric and stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural compositions containing them and their use as arthropodicides:



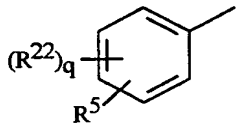
I

wherein

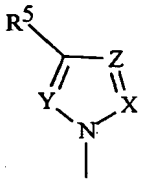
Q^1 is O, S, NR^{17}, $OCR^{18}R^{19}$, or $NR^{17}CR^{18}R^{19}$; wherein when Q^1 is $OCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$, then Q^1 is attached to the pyrimidine through the O or N atom respectively;

Q^2 is S, CR^3R^4, $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$; wherein when Q^2 is $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$ then Q^2 is attached to the pyrimidine through the O, S or N atom respectively;

J is



or



J^1 J^2

X, Y and Z are each independently N or CR^{22};

R^1 and R^2 are each independently H, C_1-C_4 alkyl, halogen, NR^7R^8, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkylthio or nitro;

R^3 and R^4 are each independently H, halogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl or cyano; or R^3 and R^4 are taken together with the attached carbon to make a carbonyl;

each R^5 is independently H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11};

each R^6 and each R^{22} is independently H, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_1-C_4 alkoxy, NR^{17} or $S(O)_nR^9$;

R^7 and R^8 are each independently H, C_1-C_4 alkyl, C_3-C_6 alkenyl, C_3-C_6 alkynyl, COR^{10}, CO_2R^{11}, CHO, SO_2R^{12} or OR^{13};

each R^9 is independently C_1-C_4 alkyl or C_1-C_4 haloalkyl;

each R^{10} is independently C_1-C_6 alkyl, phenyl optionally substituted by R^6, C_1-C_6 haloalkyl, CO_2R^{14}, C_1-C_6 alkoxyalkyl, C_2-C_4 alkenyl, C_2-C_6 alkynyl, C_2-C_6 cyanoalkyl or $NR^{15}R^{16}$;

R^{11} and R^{12} are each independently C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl or C_2-C_6 alkynyl;

R^{13} and R^{17} are each independently C_1-C_4 alkyl, H, COR^{10} or CO_2R^{11};

each R^{14} is independently C_1-C_4 alkyl;

each R^{15} is independently H, C_1-C_4 alkyl, C_1-C_4 alkoxy or phenyl optionally substituted by R^6;

R^{16} and R^{19} are each independently H or C_1-C_4 alkyl;

each R^{18} is independently H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, or cyano;

n is 0-2;

p is 0-4; and

q is 0-4;

provided that when Q^2 is $NR^{17}CR^{18}R^{19}$, then J is J^2.

In the above recitations, the term "alkyl", used either alone or in compound words such as "alkylthio" or "haloalkyl" includes straight-chain or branched alkyl, such as methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl, pentyl or hexyl isomers. "Alkenyl" includes straight-chain or branched alkenes such as ethenyl, 1-propenyl, 2-propenyl, and the different butenyl, pentenyl and hexenyl isomers. "Alkenyl" also includes polyenes such as 1,2-propadienyl and 2,4-hexadienyl. "Alkynyl" includes straight-chain or branched alkynes such as ethynyl, 1-propynyl, 2-propynyl and the different butynyl, pentynyl and hexynyl isomers. "Alkynyl" can also include moieties comprised of multiple triple bonds such as 2,5-hexadiynyl. "Alkoxy" includes, for example, methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers. "Alkoxyalkyl" denotes alkoxy substitution on alkyl. Examples of "alkoxyalkyl" include CH_3OCH_2, $CH_3OCH_2CH_2$, $CH_3CH_2OCH_2$, $CH_3CH_2CH_2CH_2OCH_2$ and $CH_3CH_2OCH_2CH_2$. "Cyanoalkyl" denotes an alkyl group substituted with one cyano group. Examples of "cyanoalkyl" include $NCCH_2$, $NCCH_2CH_2$ and $CH_3CH(CN)CH_2$. The term "halogen", either alone or in compound words such as "haloalkyl", includes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl", said alkyl may be partially or fully substituted with halogen atoms which may be the same or different. Examples of "haloalkyl" include F_3C, $ClCH_2$, CF_3CH_2 and CF_3CCl_2. The term "haloalkoxy" is defined analogously to the term "haloalkyl".

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 6. For example, C_1-C_4 alkyl designates methyl, ethyl, *n*-propyl, *i*-propyl, or the different butyl isomers. In the above recitations, when a compound of Formula I is comprised of one or more heterocyclic rings, all substituents are attached to these rings through any available carbon or nitrogen by replacement of a hydrogen on said carbon or nitrogen.

When a compound is substituted with a substituent bearing a subscript that indicates the number of said substituents can exceed 1, said substituents (when they exceed 1) are independently selected from the group of defined substituents. Further, when the subscript indicates a range, e.g. $(R)_{i-j}$, then the number of substituents may be selected from the integers between i and j inclusive.

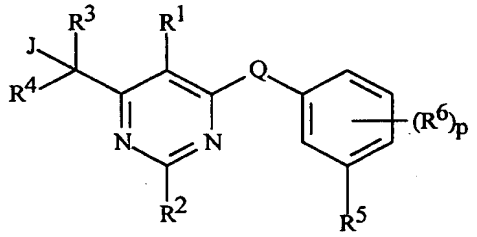
When a group contains a substituent which can be hydrogen, for example R^1 or R^6, then, when this substituent is taken as hydrogen, it is recognized that this is equivalent to said group being unsubstituted.

One skilled in the art will appreciate that not all nitrogen containing heterocycles can form *N*-oxides since the nitrogen requires an available lone pair for oxidation to the oxide; one skilled in the art will recognize those nitrogen containing heterocycles which can form *N*-oxides. One skilled in the art will also recognize that tertiary amines can form *N*-oxides. Synthetic methods for the preparation of *N*-oxides of heterocycles and tertiary amines are very well known by one skilled in the art including the oxidation of heterocycles and tertiary amines with peroxy acids such as peracetic and *m*-chloroperbenzoic acid (MCPBA), hydrogen peroxide, alkyl hydroperoxides such as *t*-butyl hydroperoxide, sodium perborate, and dioxiranes such as dimethydioxirane. These methods for the preparation of *N*-oxides have been extensively described and reviewed in the literature, see for example: T. L. Gilchrist in *Comprehensive Organic Synthesis*, vol. 7, pp 748-750, S. V. Ley, Ed., Pergamon Press; M. Tisler and B. Stanovnik in *Comprehensive Heterocyclic Chemistry*, vol. *3*, pp 18-20, A. J. Boulton and A. McKillop, Eds., Pergamon Press; M. R. Grimmett and B. R. T. Keene in *Advances in Heterocyclic Chemistry*, vol. *43*, pp 149-161, A. R. Katritzky, Ed., Academic Press; M. Tisler and B. Stanovnik in *Advances in Heterocyclic Chemistry*, vol. *9*, pp 285-291, A. R. Katritzky and A. J. Boulton, Eds., Academic Press; and G. W. H. Cheeseman and E. S. G. Werstiuk in *Advances in Heterocyclic Chemistry*, vol. *22*, pp 390-392, A. R. Katritzky and A. J. Boulton, Eds., Academic Press.

Compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers, atropisomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active and/or may exhibit beneficial effects when enriched relative to the other stereoisomer(s) or when separated from the other stereoisomer(s). Additionally, the skilled artisan knows how to separate, enrich, and/or to selectively prepare said stereoisomers. Accordingly, the present invention comprises compounds selected from Formula I, *N*-oxides and agriculturally suitable salts thereof. The compounds of the invention may be present as a mixture of stereoisomers, individual stereoisomers, or as an optically active form.

The salts of the compounds of the invention include acid-addition salts with inorganic or organic acids such as hydrobromic, hydrochloric, nitric, phosphoric, sulfuric, acetic, butyric, fumaric, lactic, maleic, malonic, oxalic, propionic, salicylic, tartaric, 4-toluenesulfonic or valeric acids. The salts of the compounds of the invention also include those formed with organic bases (e.g., pyridine, ammonia, or triethylamine) or inorganic bases (e.g., hydrides, hydroxides, or carbonates of sodium, potassium, lithium, calcium, magnesium or barium) when the compound contains an acidic group such as a carboxylic acid or phenol.

Of note are compounds of Formula Ie, including all geometric and stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural compositions containing them and their use as arthropodicides:



Ie

wherein

Q is O, S or NR^{17};

R^1 and R^2 are each independently H, C_1-C_4 alkyl, halogen, NR^7R^8, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkylthio or nitro;

R^3 and R^4 are each independently H, halogen, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl or cyano; or R^3 and R^4 are taken together with the attached carbon to make a carbonyl;

each R^5 is independently halogen, C_1-C_4 alkyl, C_1-C_4 haloalkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11};

each R^6 is independently H, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_1-C_4 alkoxy, or $S(O)_nR^9$;

R^7 and R^8 are each independently H, C_1-C_4 alkyl, C_3-C_6 alkenyl, C_3-C_6 alkynyl, COR^{10}, CO_2R^{11}, CHO, SO_2R^{12} or OR^{13};

each R^9 is independently C_1-C_4 alkyl or C_1-C_4 haloalkyl;

each R^{10} is independently C_1-C_6 alkyl, phenyl optionally substituted by R^6, C_1-C_6 haloalkyl, CO_2R^{14}, C_1-C_6 alkoxyalkyl, C_2-C_4 alkenyl, C_2-C_6 alkynyl, C_2-C_6 cyanoalkyl or $NR^{15}R^{16}$;

R^{11} and R^{12} are each independently C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl or C_2-C_6 alkynyl;

R^{13} and R^{17} are each independently C_1-C_4 alkyl, H, COR^{10} or CO_2R^{11};

each R^{14} is independently C_1-C_4 alkyl;

each R^{15} is independently H, C_1-C_4 alkyl, C_1-C_4 alkoxy or phenyl optionally substituted by R^6;

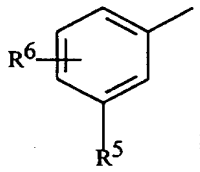
each R^{16} is independently H or C_1-C_4 alkyl;

n is 0-2;

p is 0-4;

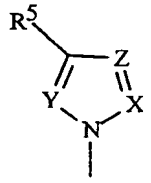
J is J^1 or J^2;

J^1 is



;

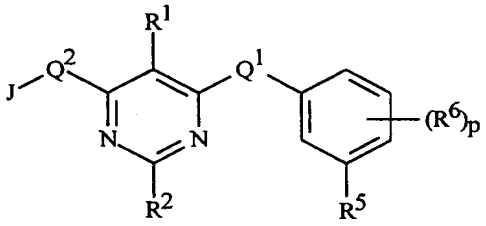
J^2 is



; an

X, Y and Z are each independently N or CR^6.

Also of note are compounds of Formula If, including all geometric and stereoisomers, *N*-oxides, and agriculturally suitable salts thereof, agricultural compositions containing them and their use as arthropodicides:



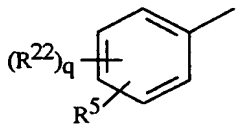
If

wherein

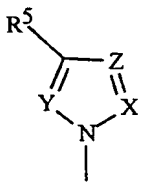
Q^1 is O, S, NR^{17}, $OCR^{18}R^{19}$, or $NR^{17}CR^{18}R^{19}$; wherein when Q^1 is $OCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$, then Q^1 is attached to the pyrimidine through the O or N atom respectively;

Q^2 is S, CR^3R^4, $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$; wherein when Q^2 is $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$ then Q^2 is attached to the pyrimidine through the O, S or N atom respectively;

J is



or



J^1 J^2

X, Y and Z are each independently N or CR^{22};

R^1 and R^2 are each independently H, C_1-C_4 alkyl, halogen, NR^7R^8, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkylthio or nitro;

R^3 and R^4 are each independently H, halogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl or cyano; or R^3 and R^4 are taken together with the attached carbon to make a carbonyl;

each R^5 is independently H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11};

each R^6 and each R^{22} is independently H, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_1-C_4 alkoxy, NR^{17} or $S(O)_nR^9$;

R^7 and R^8 are each independently H, C_1-C_4 alkyl, C_3-C_6 alkenyl, C_3-C_6 alkynyl, COR^{10}, CO_2R^{11}, CHO, SO_2R^{12} or OR^{13};

each R^9 is independently C_1-C_4 alkyl or C_1-C_4 haloalkyl;

each R^{10} is independently C_1-C_6 alkyl, phenyl optionally substituted by R^6, C_1-C_6 haloalkyl, CO_2R^{14}, C_1-C_6 alkoxyalkyl, C_2-C_4 alkenyl, C_2-C_6 alkynyl, C_2-C_6 cyanoalkyl or $NR^{15}R^{16}$;

R^{11} and R^{12} are each independently C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl or C_2-C_6 alkynyl;

R^{13} and R^{17} are each independently C_1-C_4 alkyl, H, COR^{10} or CO_2R^{11};

each R^{14} is independently C_1-C_4 alkyl;

each R^{15} is independently H, C_1-C_4 alkyl, C_1-C_4 alkoxy or phenyl optionally substituted by R^6;

R^{16} and R^{19} are each independently H or C_1-C_4 alkyl;

each R^{18} is independently H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, or cyano;

n is 0-2;

p is 0-4; and

q is 0-4.

Preferred compounds for reasons of better activity and/or ease of synthesis are:

Preferred 1. Compounds of Formula I above, *N*-oxides and agriculturally suitable salts thereof, wherein:

J is J^1;

R^1 and R^2 are H;

R^5 is C_1-C_2 haloalkyl;

each R^6 and each R^{22} is halogen; and

R^3 and R^4 are either each H or taken together with the attached carbon as a carbonyl.

Preferred 2. Compounds of Formula I above, *N*-oxides and agriculturally suitable salts thereof, wherein:

J is J^2;

R^1 and R^2 are H;

R^5 is C_1 to C_2 haloalkyl;

each R^6 and each R^{22} is halogen;

R^3 and R^4 are each H; and

Y is N, X is CH and Z is CR^{22}.

Most preferred are compounds of Preferred 1 selected from the group:

4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]pyrimidine;

4-[4-chloro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]pyrimidine;

[6-[4-fluoro-3-(trifluoromethyl)phenoxy]-4-pyrimidinyl][4-fluoro-3-(trifluoromethyl)phenyl]methanone;

4-[4-fluoro-3-(trifluoromethyl)phenyl]-6-[3-(trifluoromethyl)-phenyl]methoxypyrimidine;

4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-5-pyrimidinamine;

4-[(3,4-difluorophenyl)methoxy]-6-[4-fluoro-3-(trifluoromethyl)phenoxy]pyrimidine and

4-[4-fluoro-3-(trifluoromethyl)phenoxy]- 6-[(4-fluorophenyl)thio]pyrimidine.

This invention also relates to arthropodicidal compositions comprising arthropodicidally effective amounts of the compounds of the invention and at least one of a surfactant, a solid diluent or a liquid diluent. The preferred compositions of the present invention are those which comprise the above preferred compounds.

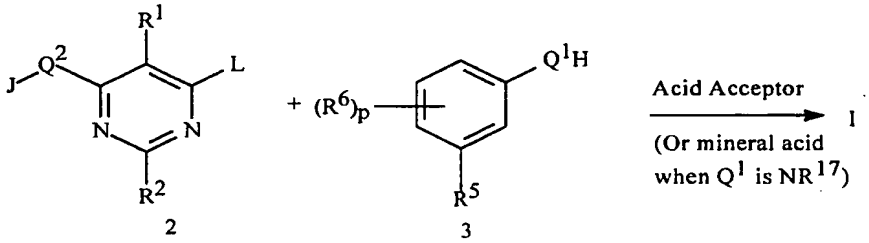
This invention also relates to a method for controlling arthropods comprising contacting the arthropods or their environment with an arthropodicidally effective amount of the compounds of the invention (e.g., as a composition described herein). The preferred methods of use are those involving the above preferred compounds.

DETAILS OF THE INVENTION

The compounds of Formula I can be prepared by one or more of the following methods and variations as described in Schemes 1-10. The definitions of J, Q^1, Q^2, R^1 through R^{22}, X, Y, Z, n and p in the compounds of Formulae 1-15 below are as defined above in the Summary of the Invention. Compounds of Formulae Ia-Id are various subsets of the compounds of Formula I, and all substituents for Formulae Ia-Id are as defined above for Formula I.

Scheme 1 illustrates the preparation of compounds of Formula I by displacement of a pyrimidine of Formula 2 with a nucleophile of Formula 3 in the presence of a base. Pyrimidines of Formula 2 in which L is a halogen or sulfone react with nucleophiles of Formula 3 in the presence of a variety of acid acceptors and in a variety of solvents to give the desired compounds of Formula I. Preferred acid acceptors include alkali carbonates, hydroxides and hydrides with potassium carbonate being the most preferred acid acceptor. Many solvents are acceptable such as acetone, methylethylketone, acetonitrile, dimethylformamide, dimethylacetamide, and dimethylsulfoxide. In some instances aqueous solvents or lower alcohols may be used. The reaction may be run at temperatures from 0 to 150 °C with temperatures from 20 to 80 °C being preferred. When Q^1 is NR^{17} the reaction may also be run in acidic media such as aqueous mineral acids or homogeneous mixtures of aqueous acids with miscible organic solvents. A preferred method for using anilines (Formula 3 wherein Q^1 is NR^{17}) is to carry out the reaction in aqueous acetone containing hydrochloric acid.

Scheme 1



2

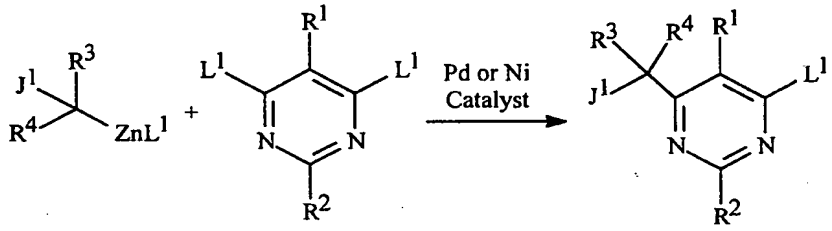
3

L is halogen or $SO_2(C_1\text{-}C_4$ alkyl)

Q^1 is O, S, NR^{17} or $OCR^{18}R^{19}$

As shown in Scheme 2, compounds of Formula 2a (compounds of Formula 2 wherein J is J^1 and Q^2 is CR^3R^4) can be readily prepared by the coupling of a zinc species of Formula 4 with a halogenopyrimidine of Formula 5. The coupling reaction can be catalyzed by either nickel or palladium complexes. The preferred complexes for this transformation are tetrakis(triphenylphosphine)palladium and dichloro-bis(triphenylphosphine)palladium. The catalyst may be present in an amount from 0.5-10% relative to the pyrimidine and zinc reagent. The reaction may be run in a variety of solvents with aprotic solvents such as acetonitrile, dimethylformamide, and tetrahydrofuran being preferred. The reaction, depending upon the substituents on the pyrimidine ring, may be done at temperatures ranging from 20 to 120 °C. Compounds of Formula 5 are generally commercially available or can be made by known methods (see D. J. Brown in *The Pyrimidines* in E. C. Taylor, editor, *The Chemistry of Heterocyclic Compounds, Vol 16*, **1957**,: Supplement I, **1967** and Supplement II, **1985**; Wiley, New York).

Scheme 2

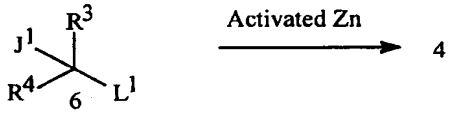


4 5 2a

Each L^1 is independently halogen

Scheme 3 illustrates the synthesis of zinc reagents of Formula 4 from halogenated methylbenzenes of Formula 6. The substituted halide of Formula 6 is reacted with activated zinc (see Jubert and Knochel, *J. Org, Chem.* **1992**,. *57*, p 5425 and Knochel *et. al.*, *Tetrahedron* **1998**, *54*, p 8275) in a suitable solvent such as tetrahydrofuran, acetonitrile, *N,N*-dimethylformamide, dimethoxyethane or other aprotic solvent. Reaction temperatures may range from 0 to 80 °C.

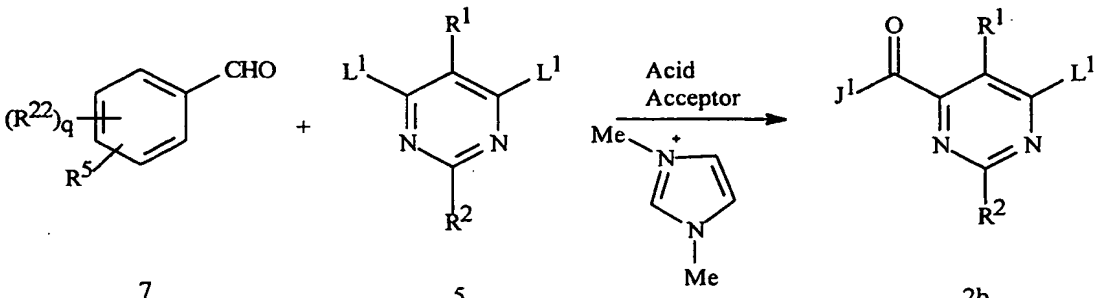
Scheme 3



L^1 is halogen

Compounds of Formula 2b (compounds of Formula 2 wherein Q^2 is C(=O), J is J^1 and L^1 is halogen) can be prepared by the condensation of pyrimidines of Formula 5 and aldehydes of Formula 7 in the presence of an imidazolium catalyst of Formula 8 as shown in Scheme 4. This reaction is carried out in the presence of a strong base such as an alkali hydride, preferrably sodium hydride, in solvents such as dichloromethane, dioxane, tetrahydrofuran, benzene, toluene or other aprotic solvent. The reaction may be carried out at temperatures between 0 and 120 °C. A wide variety of azolium salts catalyze this transformation and a number are described by Miyashita (*Heterocycles*, **1996**, *43*, 509-512 and references cited therein). A preferred catalyst is 1,3-dimethylimidazolium iodide which may be present in a 10 to 100% catalyst load.

Scheme 4

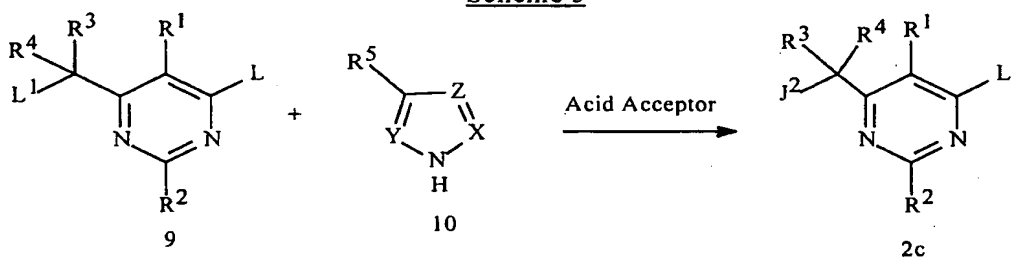


7 5 8 2b

Each L^1 is independently halogen

As shown in Scheme 5, compounds of Formula 2c (compounds of Formula 2 wherein J is J^2 and Q^2 is CR^3R^4) may be prepared by the reaction of a pyrimidine of Formula 9 with a heterocycle of Formula 10 in the presence of an acid acceptor. Preferred acid acceptors are alkali carbonates, hydroxides and hydrides with potassium carbonate being the most preferred acid acceptor. Many solvents are useful such as acetone, methylethylketone, acetonitrile, dimethylformamide, dimethylacetamide, and dimethylsulfoxide. In some instances aqueous solvents or lower alcohols may be used. The reaction may be run at temperatures from 0 to 150 °C with temperatures from 20 to 80 °C being preferred.

Scheme 5

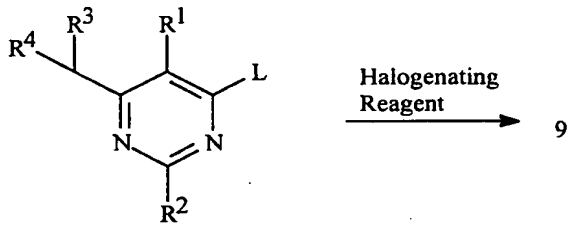


9 10 2c

L^1 is halogen
L is halogen or SO_2C_1-C_4 alkyl

Pyrimidines of Formula 9 may be prepared according to Scheme 6. Treatment of pyrimidines of Formula 11 with a suitable halogenating reagent gives the pyrimidine of Formula 9. Preferred halogenating agents include bromine, *N*-bromosuccinimide, sulfuryl chloride, and *N*-chlorosuccinimide. In the case of bromine the preferred solvents are lower carboxylic acids such as acetic acid. Polar aprotic solvents such as dimethylformamide are preferred in reactions involving *N*-halosuccinimides. The halogenation may be carried out at temperatures ranging from 20 to 120 °C.

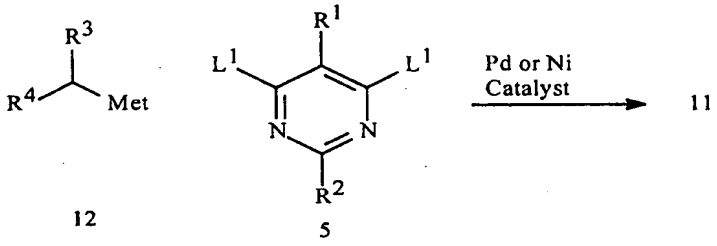
Scheme 6



11 L is halogen or SO_2C_1-C_4alkyl

Many compounds of Formula 11 are known in the art and others as illustrated by Scheme 7 can be prepared by the reaction of known organometallic species of Formula 12 with pyrimidines of Formula 5. The coupling reaction can be catalyzed by either nickel or palladium complexes. The preferred complexes for this transformation are tetrakis(triphenylphosphine)palladium and dichloro-bis(triphenylphosphine)palladium. The catalyst may be present in an amount from 0.5-10 % relative to the pyrimidine and zinc reagent. The reaction may be run in a variety of solvents with aprotic solvents such as acetonitrile, dimethylformamide, and tetrahydrofuran being preferred. The reaction depending upon the substituents on the pyrimidine ring may be done at temperatures ranging from 20 to 120 °C.

Scheme 7



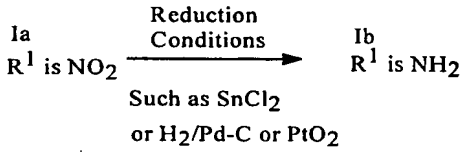
12 5

Met is Mg, Li, Zn, Sn
Each L^1 is independently halogen

As indicated in Scheme 8, compounds of Formula Ib (compounds of Formula I in which R^1 is NH_2) may be synthesized by reduction of nitropyrimidines of Formula Ib (compounds of Formula I in which R^1 is NO_2.) The reduction of nitro groups to amines is well known in the art and can be accomplished by many reagents and techniques as illustrated by Larock, *Comprehensive Organic Transformations*, VCH, **1989**, p 411 to 417 and March *Advanced Organic Chemistry*, Wiley, **1992,** 1216-18 and 1232-33. In the present example the preferred technique is catalytic hydrogenation using palladium on carbon or platinum oxide as catalyst. A wide variety of ethers, amides, alcohols and esters can be used

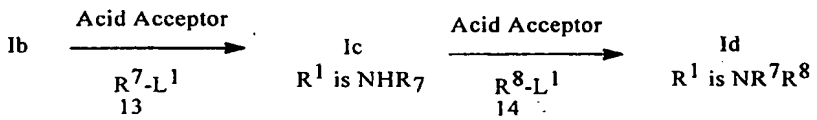
as solvents in this process with tetrahydrofuran or ethyl acetate being preferred. This transformation can be carried out at temperatures from 0 to 100 °C, with 20-30 °C being preferred, under 1-100 atmospheres of hydrogen. Another useful method is to use tin (II) chloride as the reductant in ethyl acetate or ethanol as solvent. This reaction can be carried out at temperatures between 0 and 80 °C.

Scheme 8



Compounds of Formula Ic (compounds of Formula I in which R^1 is NR^7R^8) can be made as indicated in Scheme 9. Compounds of Formula Ib may be alkylated, acylated or sulfonylated by alkyl halides, acyl halides or sulfonyl halides of Formula 13, respectively, in the presence of an acid acceptor. The reaction may be carried out with an excess of the compound of Formula 13 to yield compounds of Formula Id where R^7 and R^8 are the same. It also may be carried out in a stepwise manner to yield first a compound of Formula Ic in which R^1 is NR^7R^8, R^8 is hydrogen, and R^7 is other than hydrogen. In a second iteration of the process a second compound of Formula 14 may be reacted to yield the compound of Formula Id where R^1 is NR^7R^8 and both R^7 and R^8 are other than hydrogen. Preferred acid acceptors are tertiary amines, alkali carbonates, hydroxides and hydrides with potassium carbonate and triethylamine being the most preferred acid acceptors. Many solvents are acceptable such as acetone, methyl ethylketone, acetonitrile, dimethylformamide, dimethylacetamide, and dimethylsulfoxide. In some instances aqueous solvents or lower alcohols may be used. The reaction may be run at temperatures from 0 to 150 °C with temperatures from 20 to 80 °C being preferred.

Scheme 9

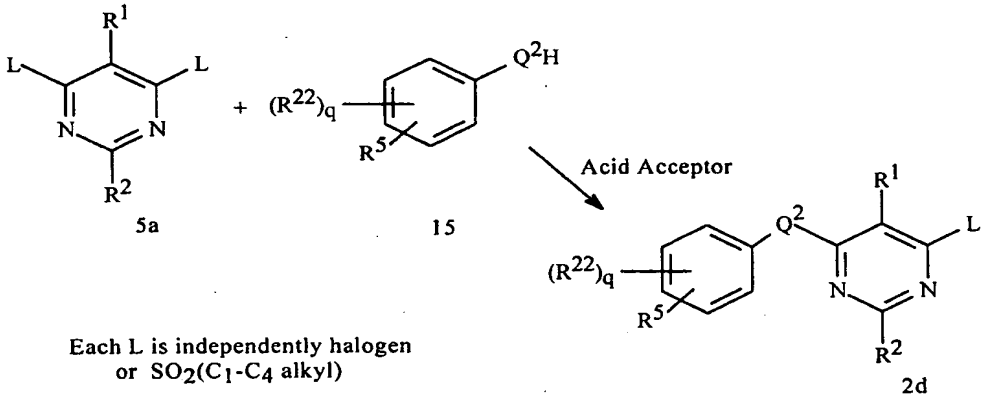


(each L^1 is independently halogen)

Scheme 10 illustrates the preparation of compounds of Formula 2d by displacement of a pyrimidine of Formula 5a with a nucleophile of Formula 15 in the presence of a base. Pyrimidines of Formula 5a in which L is a halogen or sulfone react with nucleophiles of

Formula 15 in the presence of a variety of acid acceptors and in a variety of solvents to give the desired compounds of Formula 2d. Preferred acid acceptors include alkali carbonates, hydroxides, alkoxides and hydrides with potassium carbonate being the most preferred acid acceptor. Organic tertiary amines such as triethylamine are also acceptable bases for this reaction. Many solvents are acceptable such as acetone, methylethylketone, acetonitrile, dimethylformamide, dimethylacetamide, and dimethylsulfoxide. In some instances aqueous solvents or lower alcohols may be used. The reaction may be run at temperatures from 0 to 150 °C with temperatures from 20 to 80 °C being preferred. When Q^2 is $OCR^{18}R^{19}$ or $SCR^{18}R^{19}$ the preferred bases are alkali hydrides such as sodium hydride or alkali alkoxides such as potassium t-butoxide. In these cases solvents such as dimethylformamide, dimethylacetamide, and tetrahydrofuran are preferred. When Q^2 is $NR^{17}CR^{18}R^{19}$ the preferred bases are tertiary amines with triethylamine being the most preferred.

Scheme 10



Each L is independently halogen or $SO_2(C_1\text{-}C_4$ alkyl)

Q^2 is S, $OCR^{18}R^{19}$, NR^{17} $CR^{18}R^{19}$ or $SCR^{18}R^{19}$

It is recognized that some reagents and reaction conditions described above for preparing compounds of Formula I may not be compatible with certain functionalities present in the intermediates. In these instances, the incorporation of protection/deprotection sequences or functional group interconversions into the synthesis will aid in obtaining the desired products. The use and choice of the protecting groups will be apparent to one skilled in chemical synthesis (see, for example, Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, **1991**). One skilled in the art will recognize that, in some cases, after the introduction of a given reagent as it is depicted in any individual scheme, it may be necessary to perform additional routine synthetic steps not described in detail to complete the synthesis of compounds of Formula I. One skilled in the art will also recognize that it may be necessary to perform a combination of the steps illustrated in the above schemes in an order other than that implied by the particular sequence presented to prepare the compounds of Formula I.

One skilled in the art will also recognize that compounds of Formula I and the intermediates described herein can be subjected to various electrophilic, nucleophilic, radical, organometallic, oxidation, and reduction reactions to add substituents or modify existing substituents.

Without further elaboration, it is believed that one skilled in the art using the preceding description can utilize the present invention to its fullest extent. The following Examples are, therefore, to be construed as merely illustrative, and not limiting of the disclosure in any way whatsoever. Percentages are by weight except for chromatographic solvent mixtures or where otherwise indicated. Parts and percentages for chromatographic solvent mixtures are by volume unless otherwise indicated. ^{1}H NMR spectra are reported in ppm downfield from tetramethylsilane; s is singlet, d is doublet, t is triplet, q is quartet, m is multiplet, dd is doublet of doublets, dt is doublet of triplets, br s is broad singlet.

EXAMPLE 1

Preparation of 4-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-6-[3-(trifluoromethyl)phenoxy]pyrimidine

Step A: Preparation of 4-chloro-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]pyrimidine

Zinc powder (1.3 g, 20 mmol) was suspended in tetrahydrofuran (10 mL) and treated with dibromoethane (2 drops) and heated at reflux for 5 minutes. Trimethylsilyl chloride (2 drops) was added and the reaction was heated at reflux for 5 minutes. 4-Fluoro-3-trifluoromethylbenzyl bromide (2.5 g, 10 mmol) in tetrahydrofuran (20 mL) was then added dropwise with a corresponding exotherm slowly to reflux during the addition. The mixture was heated at reflux for 20 minutes more. The zinc was allowed to settle and the supernatant amount was drawn into a syringe and transferred to a solution of 4,6-dichloropyrimidine (1.49 g, 10 mmol) and dichloro-bis(triphenylphosphine)palladium (100 mg, 0.14 mmol) dissolved in tetrahydrofuran (10 mL). The reaction mixture was heated at reflux for 3 hours and allowed to stir at 25 °C overnight. The mixture was diluted with water (50 mL) and extracted with ethyl acetate (2 X 50 mL). The combined extracts were dried over magnesium sulfate. The residue was subjected to chromatography on silica gel using hexanes/ethyl acetate (9:1) as eluent. Appropriate fractions were pooled to give the titled compound of Step A (0.75 g) as an oil. ^{1}H NMR ($CDCl_3$), δ 4.2 (s,2H), 7.15-7.25 (m,2H), 7.42-7.55 (m,2H), 8.95 (s,1H).

Step B: Preparation of 4-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-6-[3-(trifluoromethyl)phenoxy]pyrimidine

The title compound of Step A (0.38 g, 1.3 mmol) was dissolved in acetonitrile (25 mL) and treated with 3-trifluoromethylphenol (0.18 g, 1.1 mmol) followed by potassium carbonate (0.7 g, 5 mmol). The mixture was heated at reflux for 6 hours and then filtered.

The residue was subjected to chromatography on silica gel using hexanes/ethyl acetate (85:15) as eluent. Appropriate fractions were pooled to give 4-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-6-[3-(trifluoromethyl)phenoxy]pyrimidine, a compound of the invention (0.38 g) as an oil. 1H NMR ($CDCl_3$), δ 4.11 (s,2H), 6.75 (s,1H), 7.18 (t,1H), 7.28-7.38 (m,1H), 7.42 (s,1H), 7.43-7.60 (m,2H), 8.70 (s,1H).

EXAMPLE 2

Preparation of [6-[3-(trifluoromethyl)phenoxy]-4-pyrimidinyl][3-(trifluoromethyl)phenyl]methanone

Step A: Preparation of (6-chloro-4-pyrimidinyl)[3-(trifluoromethyl)phenyl]methanone

A solution of 4,6-dichloropyrimidine (3.3 g, 21.4 mmol), 3-trifluoromethylbenzaldehyde (5.0 g, 27.8 mmol), and 1,3-dimethylimidazolium iodide (2.07 g, 9.3 mmol) in dichloromethane (40 mL) was treated with sodium hydride (60% in mineral oil, 1.11 g, 27.8 mmol). The mixture exothermed to reflux after this addition. The mixture was then heated at reflux for 3 hours. The mixture was diluted with dichloromethane (50 mL) and washed with water (50 mL) followed by saturated sodium chloride solution (50 mL). The dichloromethane solution was dried over magnesium sulfate and evaporated under reduced pressure. The residue was stirred with hexanes (50 mL) and filtered. The filtrate was evaporated and subjected to chromatography on silica gel using hexanes/ethyl acetate (85:15) as eluent. Appropriate fractions were pooled and evaporated. The residue was washed with hexanes (10 mL) to give the titled compound of Step A as an oil (0.5 g) ^1H NMR ($CDCl_3$), δ 7.67 (t,1H), 7.95 (d,1H), 8.03 (s,1H), 8.35 (d,1H), 8.45 (s,1H), 9.18 (s, 1H).

Step B: Preparation of [6-[3-(trifluoromethyl)phenoxy]-4-pyrimidinyl][3-(trifluoromethyl)phenyl]methanone

The title compound of Step A (0.40 g, 1.4 mmol) was dissolved in acetonitrile (15 mL) and treated with 3-trifluoromethylphenol (0.2 g, 1.2 mmol) followed by potassium carbonate (0.59 g, 5 mmol). The mixture was stirred at room temperature overnight. The solid was removed by filtration and the filtrate was evaporated. The residue was subjected to column chromatography on silica gel using hexanes/ethyl acetate (85:15) as eluent to give [6-[3-(trifluoromethyl)phenoxy]-4-pyrimidinyl][3-(trifluoromethyl)phenyl]methanone, a compound of the invention (0.30 g) as an oil. ^1H NMR ($CDCl_3$) δ 7.38-7.45 (m,1H), 7.49 (s,1H), 7.61 (d,3H), 7.62-7.72 (m,1H), 7.90 (d,1H), 8.38 (d,1H), 8.44 (s,1H), 8.92 (s,1H).

EXAMPLE 3

Preparation of *N*-[4-fluoro-3-(trifluoromethyl)phenyl]-6-[[3-(trifluormethyl)phenyl]methyl]-4-pyrimidinamine

4-Chloro-6-(3-trifluoromethylbenzyl)pyrimidine (0.65 g, 2.4 mmol), prepared by the same procedure as Example 1, Step A by using 3-trifluoromethylbenzyl bromide in place of

4-fluoro-3-trifluoromethylbenzyl bromide, was combined with acetone (50 mL) and water (50 mL). 4-Fluoro-3-trifluoromethylaniline (0.42 g, 2.4 mmol) and concentrated hydrochloric acid (0.5 mL) were added and the mixture was heated at reflux for 16 h. The cooled reaction mixture was made basic by the addition of concentrated ammonium hydroxide and concentrated under reduced pressure. The residue was partitioned between diethyl ether (50 mL) and water (50 mL). The organic layer was washed with saturated aqueous sodium chloride solution 50 mL), dried over magnesium sulfate, and concentrated under reduced pressure to provide an oil which upon standing gave the titled compound, a compound of the invention as a solid (0.9 g), m.p. 102-104 °C. H^1 NMR ($CDCl_3$) δ 4.03 (s,2H), 6.32 (s,1H), 6.78 (s,1H), 7.20 (m,1H), 7.43-7.57 (m,4H), 7.58-7.68 (m,2H), 8.65 (s,1H).

EXAMPLE 4

Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenyl]-6-[3-(trifluoromethyl)-phenyl]methoxypyrimidine

Step A: Preparation of 4-chloro-6-[3-(trifluoromethyl)phenyl]methoxypyrimidine

To a solution of 4,6-dichloropyrimidine (2.0 g, 13 mmol) and 3-(trifluoromethyl)-benzyl alcohol (2.0 g, 11 mmol) stirring in 20 mL of tetrahydrofuran, sodium hydride (0.5 g, 60% in oil) was added with foaming. After stirring at room temperature overnight, the reaction mixture was partitioned between 100 mL of ethyl acetate and 30 mL of water. The separated organic layer was washed twice with water and brine, dried over magnesium sulfate, and evaporated *in vacuo* to an oily residue. Purification by flash chromatography on silica gel afforded 2.5 g of the titled compound, isolated as an oil. ^1H NMR ($CDCl_3$): δ 8.60 (s,1H), 7.70 (s, 1H), 7.65-745 (m's, 3H), 6.86 (s, 1H) 5.5 (s, 2H).

Step B: Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenyl]-6-[3-(trifluoromethyl)-phenyl]methoxypyrimidine

A stirred mixture of 4-chloro-6-[3-(trifluoromethyl)phenyl]methoxypyrimidine (700 mg, 2.4 mmol), 4-fluoro-3-(trifluoromethyl)phenol (500 mg, 2.8 mmol) and powdered potassium carbonate (1.0 g, 7.2 mmol) was heated in 8 mL of *N,N*-dimethylformamide at 80 °C for 4 hours. The reaction mixture was partitioned between 75 mL of diethyl ether and 50 mL of water. The organic layer was separated, washed with water and brine and dried over magnesium sulfate. An oily residue was obtained after removing the solvent *in vacuo*. Purification by flash chromatography on silica gel afforded 715 mg of the titled compound, isolated as an oil. ^1H NMR ($CDCl_3$): δ 8.44 (s,1H), 7.71 (s, 1H), 7.65-7.20 (m's, 6H), 6.32 (s, 1H) 5.51 (s, 2H).

EXAMPLE 5

Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-5-pyrimidinamine

Step A: Preparation of 4-chloro-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-5-nitropyrimidine

Zinc powder (6.5 g, 100 mmol) in tetrahydrofuran (50 mL) was treated with dibromoethane (3 drops) and heated briefly to reflux. Upon cooling trimethylsilyl chloride (3 drops) was added and the mixture was heated at reflux briefly. After the mixture had cooled to 45 °C 4-fluoro-3-trifluoromethylbenzyl bromide (5.23 g, 20 mmol) dissolved in tetrahydrofuran (10 mL) was added dropwise. The addition caused an exotherm to reflux. After heating for 1 h at reflux the reaction was cooled to room temperature. The excess zinc was removed by centrifugation under an inert atmosphere. The supernate was added to a solution of 4,6-dichloro-5-nitropyrimidine (5.81 g, 30 mmol) dissolved in tetrahydrofuran (50 mL). Dichloro-bis-(triphenylphosphine) palladium (150 mg) was added as catalyst and the mixture was heated to reflux for 1 h. After stirring at 25 °C overnight the mixture was evaporated to dryness and subjected to column chromatography on silica gel using hexanes/ethyl acetate (1:1) as eluent. The titled compound (1.0 g) was isolated as an oil. ^{1}H NMR ($CDCl_3$): δ 4.13 (s, 2H), 7.17 (m, 1H), 7.40-7.52 (m, 1H), 7.57 (d, 1H), 9.0 (S, 1H).

Step B: Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-5-pyrimidinamine

The compound of step A (0.65 g, 1.3 mmol) and 4-fluoro-3-trifluoromethylphenol (0.27 g, 1.5 mmol) were dissolved in tetrahydrofuran (15 mL) and treated with resin-supported 1,5,7-triazabicyclo[4.4.0]-dec-5-ene (Fluka, 2.2 mmol/g, 1.5 g, 3.3 mmol). After stirring at 25 °C for 16 h the mixture was filtered and the solvent removed under reduced pressure. The residue was suspended in acetic acid (3 mL) and water (15 mL). The mixture was heated to 50 °C and iron powder 0.3 g was added. The mixture was heated at near reflux for 3 hours and then filtered through celite. The celite was washed with dichloromethane (200 mL). The organic layer was washed with saturated aqueous sodium bicarbonate solution (50 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue subjected to column chromatography on silica gel using hexanes/ethyl acetate (7:3) as eluent. The titled compound (0.10 g) was isolated as an oil. ^{1}H NMR ($CDCl_3$): δ 3.83 (s, 2H), 4.20 (s, 2H), 7.17 (m, 1H), 7.2-7.58 (m, 5H), 8.19 (s, 1H).

EXAMPLE 6

Preparation of 4-[[(4-chlorophenyl)methyl]thio]-6-[4-fluoro-3-(trifluoromethyl)phenoxy]pyrimidine

Step A: Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-methylthiopyrimidine

A solution of 4-chloro-6-methylthiopyrimidine (1.08 g, 6.8 mmol) in dimethylformamide was treated with potassium carbonate (2.8 g, 20 mmol) and 4-fluoro-3-trifluorophenol (1.2 g, 6.6 mmol) and was heated at 90 °C for 5 h. The mixture was added to ice water (40 mL) and then filtered and washed with water to give the titled compound of step A (1.8 g). M.P. : 85-87 °C. ^{1}H NMR ($CDCl_3$): δ 8.54 (s, 1H), 7.2-7.5 (m, 3H), 6.78 (s, 1H), 2.59 (s, 3H).

Step B: Preparation of 4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-methylsulfonylpyrimidine

The compound of step A (2.5 g, 5 mmol) dissolved in dichloromethane (50 mL)was treated with m-chloroperbenzoic acid (64%, 6.4 g, 24 mmol) and stirred at 25 °C for 3h. The organic layer was diluted with dichloromethane (100 mL) and washed with saturated aqueous $NaHCO_3$ solution (200 mL). The organic layer was dried over magnesium sulfate and evaporated to give the titled compound of step B (2.3 g). ^{1}H NMR ($CDCl_3$): δ 8.9 (s, 1H), 7.7 (s, 1H), 7.5-7.2 (m, 3H), 3.3 (s, 3H).

Step C: Preparation of 4-[[(4-chlorophenyl)methyl]thio]-6-[4-fluoro-3-(trifluoromethyl)phenoxy]pyrimidine

The compound of Step B (0.67 g, 2 mmol) was dissolved in dimethylformamide (5 mL) and treated with 4-chlorobenzylmercaptan (0.32 g, 1.8 mmol) and potassium carbonate (0.7 g, 5 mmol). The mixture was stirred at 25 °C for 24h and partitioned between water (50 mL) and ether (50 mL). The ether was dried over magnesium sulfate and evaporated. The residue was subjected to column chromatography on silica gel with hexanes/ethyl acetate (9:1) as eluent. Pooling appropriate fractions provided the titled compound, a compound of the invention, (0.46 g) as a white solid. M.P.: 66-69 °C; ^{1}H NMR ($CDCl_3$): δ 8.57 (s, 1H), 7.2-7.5 (m, 7H), 6.75 (s, 1H), 4.42 (s, 3H).

By the procedures described herein together with methods known in the art, the following compounds of Tables 1 to 5 can be prepared. The following abbreviations are used in the Tables which follow: *t* is tertiary, *s* is secondary, *n* is normal, *i* is iso, *c* is cyclo, Me is methyl, Et is ethyl, Pr is propyl, *i*-Pr is isopropyl, Bu is butyl, Ph is phenyl, OMe is methoxy, OEt is ethoxy, SMe is methylthio, SEt is ethylthio, CN is cyano, NO_2 is nitro, Hex is hexyl, S(O)Me is methylsulfinyl, $S(O)_2$Me is methylsulfonyl and Ac is acetyl.

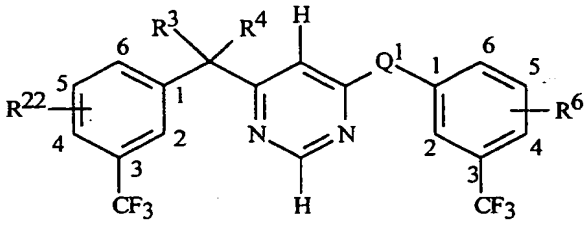


Table1

CR^3R^4 is CH_2, Q^1 is O,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CO, Q^1 is O,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN

4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CF_2, Q^1 is O,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CH_2, Q^1 is NH,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F

4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CO, Q^1 is NH,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-$SOMe_2$	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CH_2, Q^1 is S,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3

4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F
4-F	6-OC_F3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

CR^3R^4 is CO, Q^1 is S,

R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6	R^{22}	R^6
4-F	4-F	4-F	4-F	4-F	5-F	5-F	4-F	4-F	2-F
4-F	4-Cl	4-Cl	4-F	4-F	5-Cl	5-Cl	4-F	4-F	2-Cl
4-F	4-CN	4-CN	4-F	4-F	5-CN	5-CN	4-F	4-F	2-CN
4-F	4-NO_2	4-NO_2	4-F	4-F	5-NO_2	5-NO_2	4-F	4-F	2-NO_2
4-F	4-CF_3	4-CF_3	4-F	4-F	5-CF_3	5-CF_3	4-F	4-F	2-CF_3
4-F	4-OCF_3	4-OCF_3	4-F	4-F	5-OCF_3	5-OCF_3	4-F	4-F	2-OCF_3
4-F	4-Me	4-Me	4-F	4-F	5-Me	5-Me	4-F	4-F	2-Me
4-F	4-OMe	4-OMe	4-F	4-F	5-OMe	5-OMe	4-F	4-F	2-OMe
4-F	4-SMe	4-SMe	4-F	4-F	5-SMe	5-SMe	4-F	4-F	2-SMe
4-F	4-SCF_3	4-SCF_3	4-F	4-F	5-SCF_3	5-SCF_3	4-F	4-F	2-SCF_3
4-F	4-SO_2Me	4-SO_2Me	4-F	4-F	5-SO_2Me	5-SO_2Me	4-F	4-F	2-SO_2Me
4-F	4-Br	4-Br	4-F	4-F	5-Br	5-Br	4-F	4-F	2-Br
4-F	6-F	2-F	4-F	4-F	2,4-diF	6-F	4-F	2,4-diF	4-F
4-F	6-Cl	2-Cl	4-F	4-F	2,4-diCl	6-Cl	4-F	2,4-diCl	4-F
4-F	6-CN	2-CN	4-F	4-F	2,6-diF	6-CN	4-F	2,6-diF	4-F
4-F	6-NO_2	2-NO_2	4-F	4-F	4,5-diF	6-NO_2	4-F	4,5-diF	4-F
4-F	6-CF_3	2-CF_3	4-F	4-F	2,6-diCl	6-CF_3	4-F	2,6-diCl	4-F

4-F	6-OCF_3	2-OCF_3	4-F	4-F	4,5-diCl	6-OCF_3	4-F	4,5-diCl	4-F
4-F	6-Me	2-Me	4-F	4-F	5,6-diF	6-Me	4-F	5,6-diF	4-F
4-F	6-OMe	2-OMe	4-F	4-F	5.6-diCl	6-OMe	4-F	5.6-diCl	4-F
4-F	6-SMe	2-SMe	4-F	4-F	2,5-diF	6-SMe	4-F	2,5-diF	4-F
4-F	6-SCF_3	2-SCF_3	4-F	4-F	2,5-diCl	6-SCF_3	4-F	2,5-diCl	4-F
4-F	6-SO_2Me	2-SO_2Me	4-F	4-F	4,6-diF	6-SO_2Me	4-F	4,6-diF	4-F
4-F	6-Br	2-Br	4-F	4-F	4,6-diCl	6-Br	4-F	4,6-diCl	4-F

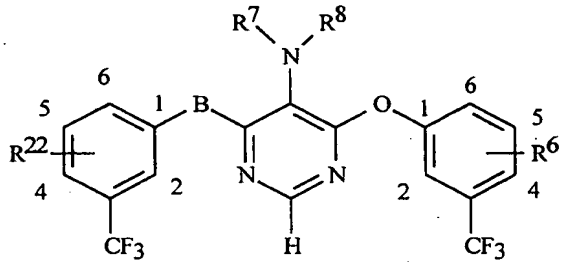


Table 2

B is CH_2, R^{22} is 4-F, R^6 is 4-F,

R^7	R^8	R^7	R^8	R^7	R^8	R^7	R^8
H	H	H	SO_2CF_3	H	$COCO_2Me$	Me	Me
H	COMe	H	CO-*n*-Pr	H	$COCH_2OMe$	COMe	COMe
H	COEt	H	CO-*i*-Pr	H	$COCH\ CH_2$	COEt	COEt
H	COOMe	H	CO-*n*-Bu	H	$COCH_2CN$	COMe	COEt
H	SO_2Me	H	CO-*i*-Bu	H	$COOCH_2CCH$	COMe	OMe
H	COPh	H	CO-*n*-Hex	H	$COOCH_2CF_3$	$CONMe_2$	COMe
H	CHO	H	COOEt	H	OH	SO_2Me	COMe
H	CONHMe	H	$CONMe_2$	H	OMe	$COCF_3$	$COCF_3$
H	CONHPh	H	$COCF_3$	H	OCOMe	Et	OH
Me	H	Me	SO_2CF_3	Me	$COCO_2Me$	H	Et
Me	COMe	Me	CO-*n*-Pr	Me	$COCH_2OMe$	H	Allyl
Me	COEt	Me	CO-*i*-Pr	Me	$COCH{=}CH_2$	H	Propargyl
Me	COOMe	Me	CO-*n*-Bu	Me	$COCH_2CN$	CONHMe	Et
Me	SO_2Me	Me	CO-*i*-Bu	Me	$COOCH_2CCH$	CONHPh	Et
Me	COPh	Me	CO-*n*-Hex	Me	$COOCH_2CF_3$	Et	Et
Me	CHO	Me	COOEt	Me	OH	COPh	COPh
Me	CONHMe	Me	$CONMe_2$	Me	OMe	$COCO_2Me$	COMe
Me	CONHPh	Me	$COCF_3$	Me	OCOMe	H	OCO_2Me

B is CO, R^{22} is 4-F, R^6 is 4-F,

R^7	R^8	R^7	R^8	R^7	R^8	R^7	R^8
H	H	H	SO_2CF3	H	$COCO_2Me$	Me	Me
H	COMe	H	CO-*n*-Pr	H	$COCH_2OMe$	COMe	COMe
H	COEt	H	CO-*i*-Pr	H	$COCH=CH_2$	COEt	COEt
H	COOMe	H	CO-*n*-Bu	H	$COCH_2CN$	COMe	COEt
H	SO_2Me	H	CO-*i*-Bu	H	$COOCH_2CCH$	COMe	OMe
H	COPh	H	CO-*n*-Hex	H	$COOCH_2CF_3$	$CONMe_2$	COMe
H	CHO	H	COOEt	H	OH	SO_2Me	COMe
H	CONHMe	H	$CONMe_2$	H	OMe	$COCF_3$	$COCF_3$
H	CONHPh	H	$COCF_3$	H	OCOMe	Et	OH
Me	H	Me	SO_2CF_3	Me	$COCO_2Me$	H	Et
Me	COMe	Me	CO-*n*-Pr	Me	$COCH_2OMe$	H	Allyl
Me	COEt	Me	CO-*i*-Pr	Me	$COCH=CH_2$	H	Propargyl
Me	COOMe	Me	CO-*n*-Bu	Me	$COCH_2CN$	CONHMe	Et
Me	SO_2Me	Me	CO-*i*-Bu	Me	$COOCH_2CCH$	CONHPh	Et
Me	COPh	Me	CO-*n*-Hex	Me	$COOCH_2CF_3$	Et	Et
Me	CHO	Me	COOEt	Me	OH	COPh	COPh
Me	CONHMe	Me	$CONMe_2$	Me	OMe	$COCO_2Me$	COMe
Me	CONHPh	Me	$COCF_3$	Me	OCOMe	H	OCO_2Me

B is CH_2, R^{22} is 4-Cl, R^6 is 4-F,

R^7	R^8	R^7	R^8	R^7	R^8	R^7	R^8
H	H	H	SO_2CF_3	H	$COCO_2Me$	Me	Me
H	COMe	H	CO-*n*-Pr	H	$COCH_2OMe$	COMe	COMe
H	COEt	H	CO-*i*-Pr	H	$COCH=CH_2$	COEt	COEt
H	COOMe	H	CO-*n*-Bu	H	$COCH_2CN$	COMe	COEt
H	SO_2Me	H	CO-*i*-Bu	H	$COOCH_2CCH$	COMe	OMe
H	COPh	H	CO-*n*-Hex	H	$COOCH_2CF_3$	$CONMe_2$	COMe
H	CHO	H	COOEt	H	OH	SO_2Me	COMe
H	CONHMe	H	$CONMe_2$	H	OMe	$COCF_3$	$COCF_3$
H	CONHPh	H	$COCF_3$	H	OCOMe	Me	OH
Me	H	Me	$SO2CF_3$	Me	$COCO_2Me$	H	Et
Me	COMe	Me	CO-*n*-Pr	Me	$COCH_2OMe$	H	Allyl
Me	COEt	Me	CO-*i*-Pr	Me	$COCH=CH_2$	H	Propargyl
Me	COOMe	Me	CO-*n*-Bu	Me	$COCH_2CN$	CONHMe	Et
Me	SO_2Me	Me	CO-*i*-Bu	Me	$COOCH_2CCH$	CONHPh	Et
Me	COPh	Me	CO-*n*-Hex	Me	$COOCH_2CF_3$	Et	Et

Me	CHO	Me	COOEt	Me	OH	COPh	COPh
Me	CONHMe	Me	$CONMe_2$	Me	OMe	$COCO_2Me$	COMe
Me	CONHPh	Me	$COCF_3$	Me	OCOMe	H	OCO_2Me

B is CH_2, R^{22} is 4-F, R^6 is 4-Cl,

R7	R8	R7	R8	R7	R8	R7	R8
H	H	H	SO_2CF3	H	COCO2Me	Me	Me
H	COMe	H	CO-*n*-Pr	H	COCH2OMe	COMe	COMe
H	COEt	H	CO-*i*-Pr	H	$COCH=CH_2$	COEt	COEt
H	COOMe	H	CO-*n*-Bu	H	$COCH_2CN$	COMe	COEt
H	SO_2Me	H	CO-*i*-Bu	H	$COOCH_2CCH$	COMe	OMe
H	COPh	H	CO-*n*-Hex	H	$COOCH_2CF_3$	$CONMe_2$	COMe
H	CHO	H	COOEt	H	OH	SO_2Me	COMe
H	CONHMe	H	$CONMe_2$	H	OMe	$COCF_3$	$COCF_3$
H	CONHPh	H	$COCF_3$	H	OCOMe	Et	OH
Me	H	Me	$SO2CF_3$	Me	$COCO_2Me$	H	Et
Me	COMe	Me	CO-*n*-Pr	Me	$COCH_2OMe$	H	Allyl
Me	COEt	Me	CO-*i*-Pr	Me	$COCH=CH_2$	H	Propargyl
Me	COOMe	Me	CO-*n*-Bu	Me	$COCH_2CN$	CONHMe	Et
Me	SO_2Me	Me	CO-*i*-Bu	Me	$COOCH_2CCH$	CONHPh	Et
Me	COPh	Me	CO-*n*-Hex	Me	$COOCH_2CF_3$	Et	Et
Me	CHO	Me	COOEt	Me	OH	COPh	COPh
Me	CONHMe	Me	$CONMe_2$	Me	OMe	$COCO_2Me$	COMe
Me	CONHPh	Me	$COCF_3$	Me	OCOMe	H	OCO_2Me

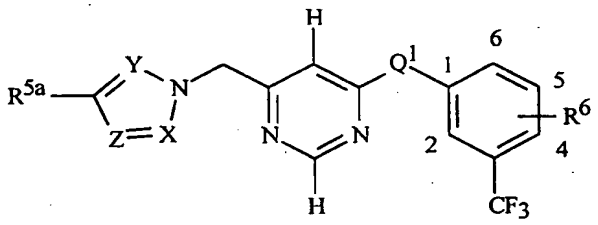


Table 3

Q^1 is O, Y is N, X is CH, Z is CR^{22},

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H

CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2Cl	H	4-Cl
CF_3	H	4-NO_2	CF3CF_2	H	4-NO_2	CF_2Cl	H	4-NO_2
CF_3	H	4-Br	CF3CF_2	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	CF3CF_2	Cl	4-F	CF_2Cl	Cl	4-F
CF_3	Cl	H	CF3CF_2	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	CF3CF_2	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	4-NO_2	CF_3CF_2	Cl	4-NO_2	CF_2Cl	Cl	4-NO_2

Q^1 is NH, Y is N, X is CH, Z is CR^{22},

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2Cl	H	4-Cl
CF_3	H	4-NO_2	CF_3CF_2	H	4-NO_2	CF_2Cl	H	4-NO_2
CF_3	H	4-Br	CF_3CF_2	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	CF_3CF_2	Cl	4-F	CF_2Cl	Cl	4-F
CF_3	Cl	H	CF_3CF_2	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	CF_3CF_2	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	4-NO_2	CF_3CF_2	Cl	4-NO_2	CF_2Cl	Cl	4-NO_2

Q^1 is O, Y is CR^{22}, X is CH, Z is N,

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2Cl	H	4-Cl
CF_3	H	4-NO_2	CF_3CF_2	H	4-NO_2	CF_2Cl	H	4-NO_2
CF_3	H	4-Br	CF_3CF_2	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	CF_3CF_2	Cl	4-F	CF_2Cl	Cl	4-F
CF_3	Cl	H	CF_3CF_2	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	CF_3CF_2	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	4-NO2	CF_3CF_2	Cl	4-NO2	CF_2Cl	Cl	4-NO_2

Q^1 is NH, Y is CR^{22}, X is CH, Z is N,

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2Cl	H	4-Cl
CF_3	H	4-NO_2	CF_3CF_2	H	4-NO_2	CF_2Cl	H	4-NO_2

CF_3	H	4-Br	$CF3CF_2$	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	$CF3CF_2$	Cl	4-F	CF_2Cl	Cl	4-F
CF_3	Cl	H	$CF3CF_2$	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	$CF3CF_2$	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	4-NO2	$CF3CF_2$	Cl	$4\text{-}NO_2$	CF_2Cl	Cl	$4\text{-}NO_2$

Q^1 is O, Y is N, X is CR^{22}, Z is N,

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2Cl	H	4-Cl
CF_3	H	$4\text{-}NO_2$	CF_3CF_2	H	$4\text{-}NO_2$	CF_2Cl	H	$4\text{-}NO_2$
CF_3	H	4-Br	CF_3CF_2	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	CF_3CF_2	Cl	4-F	CF_2Cl	Cl	4-F
CF_3	Cl	H	CF_3CF_2	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	CF_3CF2	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	$4\text{-}NO_2$	CF_3CF2	Cl	$4\text{-}NO_2$	CF_2Cl	Cl	$4\text{-}NO_2$

Q^1 is NH, Y is N, X is CR^{22}, Z is N,

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2Cl	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2Cl	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF2Cl	H	4-Cl
CF_3	H	$4\text{-}NO_2$	CF_3CF_2	H	$4\text{-}NO_2$	CF_2Cl	H	$4\text{-}NO_2$
CF_3	H	4-Br	CF_3CF_2	H	4-Br	CF_2Cl	H	4-Br
CF_3	Cl	4-F	CF_3CF_2	Cl	4-F	CF2Cl	Cl	4-F
CF_3	Cl	H	CF_3CF_2	Cl	H	CF_2Cl	Cl	H
CF_3	Cl	4-Cl	$CF3CF_2$	Cl	4-Cl	CF_2Cl	Cl	4-Cl
CF_3	Cl	$4\text{-}NO_2$	$CF3CF_2$	Cl	4-NO2	CF2Cl	Cl	$4\text{-}NO_2$

Q^1 is O, Y is CH, X is CH, Z is CR^{22},

R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6	R^{5a}	R^{22}	R^6
CF_3	H	4-F	CF_3CF_2	H	4-F	CF_2H	H	4-F
CF_3	H	H	CF_3CF_2	H	H	CF_2H	H	H
CF_3	H	4-Cl	CF_3CF_2	H	4-Cl	CF_2H	H	4-Cl
CF_3	H	$4\text{-}NO_2$	CF_3CF_2	H	$4\text{-}NO_2$	CF_2H	H	$4\text{-}NO_2$
CF_3	H	4-Br	CF_3CF_2	H	4-Br	CF_2H	H	4-Br
CF_3	Cl	4-F	CF_3CF_2	Cl	4-F	CF_2H	Cl	4-F

CF_3	Cl	H	CF_3CF_2	Cl	H	CF_2H	Cl	H
CF_3	Cl	4-Cl	CF_3CF_2	Cl	4-Cl	CF_2H	Cl	4-Cl
CF_3	Cl	4-NO_2	CF_3CF_2	Cl	4-NO_2	CF_2H	Cl	4-NO_2

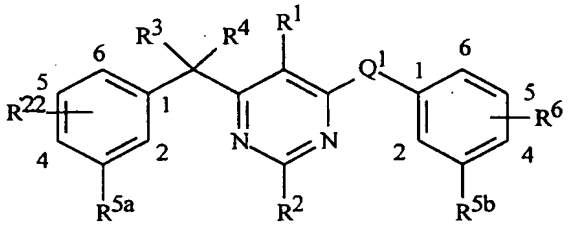


Table 4

R^1	R^2	R^3	R^4	R^{5a}	R^{22}	R^{5b}	R^6	Q^1
Me	H	H	H	CF_3	4-F	CF_3	4-F	O
Cl	H	H	H	CF_3	4-F	CF_3	4-F	O
OMe	H	H	H	CF_3	4-F	CF_3	4-F	O
CF_3	H	H	H	CF_3	4-F	CF_3	4-F	O
SMe	H	H	H	CF_3	4-F	CF_3	4-F	O
NO_2	H	H	H	CF_3	4-F	CF_3	4-F	O
H	Me	H	H	CF_3	4-F	CF_3	4-F	O
H	Cl	H	H	CF_3	4-F	CF_3	4-F	O
H	OMe	H	H	CF_3	4-F	CF_3	4-F	O
H	CF_3	H	H	CF_3	4-F	CF_3	4-F	O
H	SMe	H	H	CF_3	4-F	CF_3	4-F	O
H	NO_2	H	H	CF_3	4-F	CF_3	4-F	O
Me	H	H	H	CF_3	4-F	CF_3	4-Cl	O
Cl	H	H	H	CF_3	4-F	CF_3	4-Cl	O
OMe	H	H	H	CF_3	4-F	CF_3	4-Cl	O
CF_3	H	H	H	CF_3	4-F	CF_3	4-Cl	O
SMe	H	H	H	CF_3	4-F	CF_3	4-Cl	O
NO_2	H	H	H	CF_3	4-F	CF_3	4-Cl	O
H	Me	H	H	CF_3	4-F	CF_3	4-Cl	O
H	Cl	H	H	CF_3	4-F	CF_3	4-Cl	O
H	OMe	H	H	CF_3	4-F	CF_3	4-Cl	O
H	CF_3	H	H	CF_3	4-F	CF_3	4-Cl	O
H	SMe	H	H	CF_3	4-F	CF_3	4-Cl	O
H	Cl	H	H	CF_3	4-F	CF_3	4-Cl	O
H	H	H	H	CF_3	4-Cl	CF_3	4-F	O
H	H	H	H	Cl	4-Cl	CF_3	4-F	O
H	Cl	H	H	Cl	4-CF_3	CF_3	4-F	O

H	H	H	H	CF_3	4-CF_3	CF_3	4-F	O
H	H	H	H	Me	4-F	CF_3	4-F	O
H	H	H	H	OCF_3	4-F	CF_3	4-F	O
H	H	H	H	CF_2CF_3	4-F	CF_3	4-F	O
H	H	H	H	CF_2CF_3	4-F	CF_3	4-Cl	O
H	H	H	H	CF_2CF_3	4-F	CF_3	H	O
H	H	H	H	CF_2CF_3	H	CF_3	4-F	O
H	H	H	H	CF_3	H	CF_3	4-F	O
H	H	H	H	CF_3	4-F	CF_3	H	O
H	H	H	H	CF_2Cl	4-F	CF_3	4-F	O
H	H	H	H	CF_2Cl	4-F	CF_3	4-Cl	O
H	H	H	H	CF_2Cl	4-Cl	CF_3	4-F	O
H	H	H	H	CF_2Cl	4-F	CF_3	H	O
H	H	H	H	CF_2Cl	4-F	CF_2Cl	4-F	O
H	H	H	H	OMe	4-F	CF3	4-F	O
H	H	H	H	SF_5	H	CF_3	4-F	O
H	H	H	H	CF_3	4-F	Cl	4-Cl	O
H	H	H	H	CF_3	4-F	Cl	4-CF_3	O
H	Cl	H	H	CF_3	4-F	CF_3	4-CF_3	O
H	H	H	H	CF_3	4-F	Me	4-F	O
H	H	H	H	CF_3	4-F	OCF_3	4-F	O
H	H	H	H	CF_3	4-F	CF_2CF_3	4-F	O
H	H	H	H	CF_3	4-Cl	CF_2CF_3	4-F	O
H	H	H	H	CF_3	H	CF_2CF_3	4-F	O
H	H	H	H	CF_3	4-F	CF_2CF_3	H	O
H	H	H	H	CF_3	4-F	CF_3	H	O
H	H	H	H	CF_3	H	CF_3	4-F	O
H	H	H	H	CF_3	4-F	CF_2Cl	4-F	O
H	H	H	H	CF_3	4-Cl	CF_2Cl	4-F	O
H	H	H	H	CF_3	4-F	CF_2Cl	4-Cl	O
H	H	H	H	CF_3	H	CF_2Cl	4-F	O
H	H	H	H	CF_3	4-F	OMe	4-F	O
H	H	H	H	CF_3	4-F	SF5	H	O
H	H	H	H	CN	4-F	CF_3	4-F	O
H	H	H	H	CF_3	4-F	CN	4-F	O
H	H	H	H	SCF_3	4-F	CF_3	4-F	O
H	H	H	H	CF_3	4-F	SCF_3	4-F	O
H	H	H	H	SO_2Me	4-F	CF_3	4-F	O

H	H	H	H	CF_3	4-F	SO_2Me	4-F	O
H	H	H	H	CF_2CF_3	4-F	CF_3	4-F	NH
H	H	H	H	CF_2CF_3	4-F	CF_3	4-Cl	NH
H	H	H	H	CF_2CF_3	4-F	CF_3	H	NH
H	H	H	H	CF_2CF_3	H	CF_3	4-F	NH
H	H	H	H	CF_3	H	CF_3	4-F	NH
H	H	H	H	CF_3	4-F	CF_3	H	NH
H	H	H	H	CF_2Cl	4-F	CF_3	4-F	NH
H	H	H	H	CF_2Cl	4-F	CF_3	4-Cl	NH
H	H	H	H	CF_2Cl	4-Cl	CF_3	4-F	NH
H	H	H	H	CF_2Cl	4-F	CF_3	H	NH
H	H	H	H	CF_2Cl	4-F	CF_2Cl	4-F	NH
NH_2	H	H	H	CF_3	H	CF_3	4-F	O
NHAc	H	H	H	CF_3	H	CF_3	4-F	O
NAc_2	H	H	H	CF_3	H	CF_3	4-F	O
NHMe	H	H	H	CF_3	H	CF_3	4-F	O
NMe_2	H	H	H	CF_3	H	CF_3	4-F	O
NHCHO	H	H	H	CF_3	H	CF_3	4-F	O
NH_2	H	H	H	CF_3	4-F	CF_3	H	O
NHAc	H	H	H	CF_3	4-F	CF_3	H	O
NAc_2	H	H	H	CF_3	4-F	CF_3	H	O
NHMe	H	H	H	CF_3	4-F	CF_3	H	O
NMe_2	H	H	H	CF_3	4-F	CF_3	H	O
NHCHO	H	H	H	CF_3	4-F	CF_3	H	O
NH_2	H	H	H	CF_2CF_3	H	CF_3	4-F	O
NH_2	H	H	H	CF_3	4-F	CF_2CF_3	4-F	O
NH_2	H	H	H	CF_2Cl	4-F	CF_3	4-F	O
NH_2	H	H	H	CF_3	4-F	CF_2Cl	4-F	O
NH_2	H	H	H	CF_3	H	CF_2CF_3	4-F	O
H	H	Me	H	CF_3	4-F	CF_3	4-F	O
H	H	Me	Me	CF_3	4-F	CF_3	4-F	O
H	H	Cl	H	CF_3	4-F	CF_3	4-F	O
H	H	OMe	H	CF_3	4-F	CF_3	4-F	O
H	H	CF_3	H	CF_3	4-F	CF_3	4-F	O
H	H	CN	H	CF_3	4-F	CF_3	4-F	O
H	H	Cl	Cl	CF_3	4-F	CF_3	4-F	O

R^1	R^2	CR^3R^4	R^{5a}	R^{22}	R^{5b}	R^6	Q^1
H	H	CO	CF_2CF_3	4-F	CF_3	4-F	O
H	H	CO	CF_2CF_3	4-F	CF_3	4-Cl	O
H	H	CO	CF_2CF_3	4-F	CF_3	H	O
H	H	CO	CF_2CF_3	H	CF_3	4-F	O
H	H	CO	CF_3	H	CF_3	4-F	O
H	H	CO	CF_3	4-F	CF_3	H	O
H	H	CO	CF_2Cl	4-F	CF_3	4-F	O
H	H	CO	CF_2Cl	4-F	CF_3	4-Cl	O
H	H	CO	CF_2Cl	4-Cl	CF_3	4-F	O
H	H	CO	CF_2Cl	4-F	CF_3	H	O
H	H	CO	CF_2Cl	4-F	CF_2Cl	4-F	O

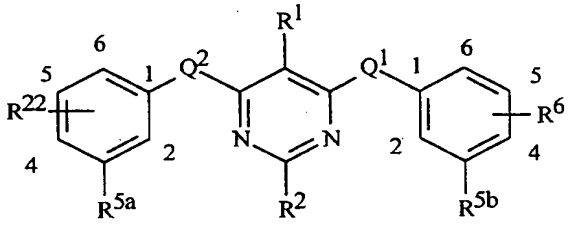


Table 5

R^1	R^2	Q^1	R^{5b}	R^6	Q^2	R^{5a}	R^{22}
H	H	O	CF_3	4-F	CH_2O	F	4-F
H	H	O	CF_3	4-F	CH_2O	F	2-F
H	H	O	CF_3	4-F	CH_2O	F	5-F
H	H	O	CF_3	4-F	CH_2O	F	6-F
H	H	O	CF_3	4-F	CH_2O	F	4-Cl
H	H	O	CF_3	4-F	CH_2O	F	2-Cl
H	H	O	CF_3	4-F	CH_2O	F	5-Cl
H	H	O	CF_3	4-F	CH_2O	F	6-Cl
H	H	O	CF_3	4-F	CH_2O	CF_3	4-F
H	H	O	CF_3	4-F	CH_2O	CF_3	2-F
H	H	O	CF_3	4-F	CH_2O	CF_3	5-F
H	H	O	CF_3	4-F	CH_2O	CF_3	6-F
H	H	O	CF_3	4-F	CH_2O	CF_3	4-Cl
H	H	O	CF_3	4-F	CH_2O	CF_3	2-Cl
H	H	O	CF_3	4-F	CH_2O	CF_3	5-Cl
H	H	O	CF_3	4-F	CH_2O	CF_3	6-Cl
H	H	O	CF_3	4-F	CH_2O	F	$4\text{-}CF_3$

H	H	O	CF_3	4-F	CH_2O	F	2-CF_3
H	H	O	CF_3	4-F	CH_2O	F	5-CF_3
H	H	O	CF_3	4-F	CH_2O	F	6-CF_3
H	H	O	CF_3	4-F	CH_2O	F	4-OCF_3
H	H	O	CF_3	4-F	CH_2O	F	2-OCF_3
H	H	O	CF_3	4-F	CH_2O	F	5-OCF_3
H	H	O	CF_3	4-F	CH_2O	F	6-OCF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	4-CF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	2-CF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	5-CF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	6-CF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	4-OCF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	2-OCF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	5-OCF_3
H	H	O	CF_3	4-F	CH_2O	CF_3	6-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	F	4-F
H	H	O	CF_3	4-Cl	CH_2O	F	2-F
H	H	O	CF_3	4-Cl	CH_2O	F	5-F
H	H	O	CF_3	4-Cl	CH_2O	F	6-F
H	H	O	CF_3	4-Cl	CH_2O	F	4-Cl
H	H	O	CF_3	4-Cl	CH_2O	F	2-Cl
H	H	O	CF_3	4-Cl	CH_2O	F	5-Cl
H	H	O	CF_3	4-Cl	CH_2O	F	6-Cl
H	H	O	CF_3	4-Cl	CH_2O	CF_3	4-F
H	H	O	CF_3	4-Cl	CH_2O	CF_3	2-F
H	H	O	CF_3	4-Cl	CH_2O	CF_3	5-F
H	H	O	CF_3	4-Cl	CH_2O	CF_3	6-F
H	H	O	CF_3	4-Cl	CH_2O	CF_3	4-Cl
H	H	O	CF_3	4-Cl	CH_2O	CF_3	2-Cl
H	H	O	CF_3	4-Cl	CH_2O	CF_3	5-Cl
H	H	O	CF_3	4-Cl	CH_2O	CF_3	6-Cl
H	H	O	CF_3	4-Cl	CH_2O	F	4-CF_3
H	H	O	CF_3	4-Cl	CH_2O	F	2-CF3
H	H	O	CF_3	4-Cl	CH_2O	F	5-CF_3
H	H	O	CF_3	4-Cl	CH_2O	F	6-CF_3
H	H	O	CF_3	4-Cl	CH_2O	F	4-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	F	2-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	F	5-OCF_3

H	H	O	CF_3	4-Cl	CH_2O	F	6-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	4-CF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	2-CF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	5-CF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	6-CF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	4-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	2-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	5-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	CF_3	6-OCF_3
H	H	O	CF_3	4-Cl	S	F	4-F
H	H	O	CF_3	4-Cl	S	F	2-F
H	H	O	CF_3	4-Cl	S	F	5-F
H	H	O	CF_3	4-Cl	S	F	6-F
H	H	O	CF_3	4-Cl	S	F	4-Cl
H	H	O	CF_3	4-Cl	S	F	2-Cl
H	H	O	CF_3	4-Cl	S	F	5-Cl
H	H	O	CF_3	4-Cl	S	F	6-Cl
H	H	O	CF_3	4-Cl	S	CF_3	4-F
H	H	O	CF_3	4-Cl	S	CF_3	2-F
H	H	O	CF_3	4-Cl	S	CF_3	5-F
H	H	O	CF_3	4-Cl	S	CF_3	6-F
H	H	O	CF_3	4-Cl	S	CF_3	4-Cl
H	H	O	CF_3	4-Cl	S	CF_3	2-Cl
H	H	O	CF_3	4-Cl	S	CF_3	5-Cl
H	H	O	CF_3	4-Cl	S	CF_3	6-Cl
NH_2	H	O	CF_3	4-F	CH_2O	F	4-F
NH_2	H	O	CF_3	4-F	CH_2O	F	2-F
NH_2	H	O	CF_3	4-F	CH_2O	F	5-F
NH_2	H	O	CF_3	4-F	CH_2O	F	6-F
NH_2	H	O	CF_3	4-F	CH_2O	F	4-Cl
NH_2	H	O	CF_3	4-F	CH_2O	F	2-Cl
NH_2	H	O	CF_3	4-F	CH_2O	F	5-Cl
NH_2	H	O	CF_3	4-F	CH_2O	F	6-Cl
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	4-F
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	2-F
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	5-F
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	6-F
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	4-Cl

NH_2	H	O	CF_3	4-F	CH_2O	CF_3	2-Cl
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	5-Cl
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	6-Cl
NH_2	H	O	CF_3	4-F	CH_2O	F	4-CF3
NH_2	H	O	CF_3	4-F	CH_2O	F	2-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	5-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	6-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	4-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	2-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	5-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	F	6-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	4-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	2-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	5-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	6-CF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	4-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	2-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	5-OCF_3
NH_2	H	O	CF_3	4-F	CH_2O	CF_3	6-OCF_3
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	4-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	2-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	5-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	6-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	4-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	2-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	5-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	F	6-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	4-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	2-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	5-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	6-F
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	4-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	2-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	5-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	6-Cl
H	H	O	CF_3	4-F	$CH(CH_3)O$	CF_3	6-Cl
H	H	O	CF_3	4-F	S	F	4-F
H	H	O	CF_3	4-F	S	F	2-F

H	H	O	CF_3	4-F	S	F	5-F
H	H	O	CF_3	4-F	S	F	6-F
H	H	O	CF_3	4-F	S	F	4-Cl
H	H	O	CF_3	4-F	S	F	2-Cl
H	H	O	CF_3	4-F	S	F	5-Cl
H	H	O	CF_3	4-F	S	F	6-Cl
H	H	O	CF_3	4-F	S	CF_3	4-F
H	H	O	CF_3	4-F	S	CF_3	2-F
H	H	O	CF_3	4-F	S	CF_3	5-F
H	H	O	CF_3	4-F	S	CF_3	6-F
H	H	O	CF_3	4-F	S	CF_3	4-Cl
H	H	O	CF_3	4-F	S	CF_3	2-Cl
H	H	O	CF_3	4-F	S	CF_3	5-Cl
H	H	O	CF_3	4-F	S	CF_3	6-Cl
H	H	O	CF_3	4-F	CH_2S	F	4-F
H	H	O	CF_3	4-F	CH_2S	F	2-F
H	H	O	CF_3	4-F	CH_2S	F	5-F
H	H	O	CF_3	4-F	CH_2S	F	6-F
H	H	O	CF_3	4-F	CH_2S	F	4-Cl
H	H	O	CF_3	4-F	CH_2S	F	2-Cl
H	H	O	CF_3	4-F	CH_2S	F	5-Cl
H	H	O	CF_3	4-F	CH_2S	F	6-Cl
H	H	O	CF_3	4-F	CH_2S	CF_3	4-F
H	H	O	CF_3	4-F	CH_2S	CF_3	2-F
H	H	O	CF_3	4-F	CH_2S	CF_3	5-F
H	H	O	CF_3	4-F	CH_2S	CF_3	6-F
H	H	O	CF_3	4-F	CH_2S	CF_3	4-Cl
H	H	O	CF_3	4-F	CH_2S	CF_3	2-Cl
H	H	O	CF_3	4-F	CH_2S	CF_3	5-Cl
H	H	O	CF_3	4-F	CH_2S	CF_3	6-Cl
H	H	CH_2O	CF_3	4-F	CH_2	F	4-F
H	H	CH_2O	CF_3	4-F	CH_2	F	2-F
H	H	CH_2O	CF_3	4-F	CH_2	F	5-F
H	H	CH_2O	CF_3	4-F	CH_2	F	6-F
H	H	CH_2O	CF_3	4-F	CH_2	F	4-Cl
H	H	CH_2O	CF_3	4-F	CH_2	F	2-Cl
H	H	CH_2O	CF_3	4-F	CH_2	F	5-Cl
H	H	CH_2O	CF_3	4-F	CH_2	F	6-Cl

H	H	CH_2O	CF_3	4-F	CH_2	CF_3	4-F
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	2-F
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	5-F
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	6-F
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	4-Cl
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	2-Cl
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	5-Cl
H	H	CH_2O	CF_3	4-F	CH_2	CF_3	6-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	F	4-F
H	H	CH_2NH	CF_3	4-F	CH_2	F	2-F
H	H	CH_2NH	CF_3	4-F	CH_2	F	5-F
H	H	CH_2NH	CF_3	4-F	CH_2	F	6-F
H	H	CH_2NH	CF_3	4-F	CH_2	F	4-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	F	2-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	F	5-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	F	6-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	4-F
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	2-F
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	5-F
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	6-F
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	4-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	2-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	5-Cl
H	H	CH_2NH	CF_3	4-F	CH_2	CF_3	6-Cl
H	H	CH_2O	CF_3	4-F	CO	F	4-F
H	H	CH_2O	CF_3	4-F	CO	F	2-F
H	H	CH_2O	CF_3	4-F	CO	F	5-F
H	H	CH_2O	CF_3	4-F	CO	F	6-F
H	H	CH_2O	CF_3	4-F	CO	F	4-Cl
H	H	CH_2O	CF_3	4-F	CO	F	2-Cl
H	H	CH_2O	CF_3	4-F	CO	F	5-Cl
H	H	CH_2O	CF_3	4-F	CO	F	6-Cl
H	H	CH_2O	CF_3	4-F	CO	CF_3	4-F
H	H	CH_2O	CF_3	4-F	CO	CF_3	2-F
H	H	CH_2O	CF_3	4-F	CO	CF_3	5-F
H	H	CH_2O	CF_3	4-F	CO	CF_3	6-F
H	H	CH_2O	CF_3	4-F	CO	CF_3	4-Cl
H	H	CH_2O	CF_3	4-F	CO	CF_3	2-Cl

H	H	CH_2O	CF_3	4-F	CO	CF_3	5-Cl
H	H	CH_2O	CF_3	4-F	CO	CF_3	6-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	F	4-F
H	H	CH_2O	CF_3	4-F	CH_2O	F	2-F
H	H	CH_2O	CF_3	4-F	CH_2O	F	5-F
H	H	CH_2O	CF_3	4-F	CH_2O	F	6-F
H	H	CH_2O	CF_3	4-F	CH_2O	F	4-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	F	2-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	F	5-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	F	6-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	4-F
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	2-F
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	5-F
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	6-F
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	4-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	2-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	5-Cl
H	H	CH_2O	CF_3	4-F	CH_2O	CF_3	6-Cl
H	H	NH	CF_3	4-F	CH_2O	F	4-F
H	H	NH	CF_3	4-F	CH_2O	F	2-F
H	H	NH	CF_3	4-F	CH_2O	F	5-F
H	H	NH	CF_3	4-F	CH_2O	F	6-F
H	H	NH	CF_3	4-F	CH_2O	F	4-Cl
H	H	NH	CF_3	4-F	CH_2O	F	2-Cl
H	H	NH	CF_3	4-F	CH_2O	F	5-Cl
H	H	NH	CF_3	4-F	CH_2O	F	6-Cl
H	H	NH	CF_3	4-F	CH_2O	CF_3	4-F
H	H	NH	CF_3	4-F	CH_2O	CF_3	2-F
H	H	NH	CF_3	4-F	CH_2O	CF_3	5-F
H	H	NH	CF_3	4-F	CH_2O	CF_3	6-F
H	H	NH	CF_3	4-F	CH_2O	CF_3	4-Cl
H	H	NH	CF_3	4-F	CH_2O	CF_3	2-Cl
H	H	NH	CF_3	4-F	CH_2O	CF_3	5-Cl
H	H	NH	CF_3	4-F	CH_2O	CF_3	6-Cl
H	H	O	CF_3	4-F	CH_2O	H	4-CF_3
H	H	O	CF_3	4-F	CH_2O	H	2-CF_3
H	H	O	CF_3	4-F	CH_2O	H	5-CF_3
H	H	O	CF_3	4-F	CH_2O	H	6-CF_3

H	H	O	CF_3	4-F	CH_2O	H	4-OCF_3
H	H	O	CF_3	4-F	CH_2O	H	2-OCF_3
H	H	O	CF_3	4-F	CH_2O	H	5-OCF_3
H	H	O	CF_3	4-F	CH_2O	H	6-OCF_3
H	H	O	CF_3	4-Cl	CH_2O	H	4-F
H	H	O	CF_3	4-Cl	CH_2O	H	2-F
H	H	O	CF_3	4-Cl	CH_2O	H	5-F
H	H	O	CF_3	4-Cl	CH_2O	H	6-F
H	H	O	CF_3	4-Cl	CH_2O	H	4-Cl
H	H	O	CF_3	4-Cl	CH_2O	H	2-Cl
H	H	O	CF_3	4-Cl	CH_2O	H	5-Cl
H	H	O	CF_3	4-Cl	CH_2O	H	6-Cl
H	H	O	CF_3	H	S	F	4-F
H	H	O	CF_3	H	S	F	2-F
H	H	O	CF_3	H	S	F	5-F
H	H	O	CF_3	H	S	F	6-F
H	H	O	CF_3	H	S	F	4-Cl
H	H	O	CF_3	H	S	F	2-Cl
H	H	O	CF_3	H	S	F	5-Cl
H	H	O	CF_3	H	S	F	6-Cl
H	H	O	CF_3	H	S	CF_3	4-F
H	H	O	CF_3	H	S	CF_3	2-F
H	H	O	CF_3	H	S	CF_3	5-F
H	H	O	CF_3	H	S	CF_3	6-F
H	H	O	CF_3	H	S	CF_3	4-Cl
H	H	O	CF_3	H	S	CF_3	2-Cl
H	H	O	CF_3	H	S	CF_3	5-Cl
H	H	O	CF_3	H	S	CF_3	6-Cl

Formulation/Utility

Compounds of this invention will generally be used as a Formulation or composition with an agriculturally suitable carrier comprising at least one of a liquid diluent, a solid diluent or a surfactant. The Formulation or composition ingredients are selected to be consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Useful Formulations include liquids such as solutions (including emulsifiable concentrates), suspensions, emulsions (including microemulsions and/or suspoemulsions) and the like which optionally can be thickened into gels. Useful Formulations further include solids such as dusts,

powders, granules, pellets, tablets, films, and the like which can be water-dispersible ("wettable") or water-soluble. The active ingredient can be (micro)encapsulated and further formed into a suspension or solid Formulation; alternatively the entire Formulation of active ingredient can be encapsulated (or "overcoated"). Encapsulation can control or delay release of the active ingredient. Sprayable Formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High-strength compositions are primarily used as intermediates for further Formulation.

The Formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up to 100 percent by weight.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Water-Dispersible and Water-soluble Granules, Tablets and Powders.	5–90	0–94	1–15
Suspensions, Emulsions, Solutions (including Emulsifiable Concentrates)	5–50	40–95	0–15
Dusts	1–25	70–99	0–5
Granules and Pellets	0.01–99	5–99.99	0–15
High Strength Compositions	90–99	0–10	0–2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All Formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth and the like, or thickeners to increase viscosity.

Surfactants include, for example, polyethoxylated alcohols, polyethoxylated alkylphenols, polyethoxylated sorbitan fatty acid esters, dialkyl sulfosuccinates, alkyl sulfates, alkylbenzene sulfonates, organosilicones, *N,N*-dialkyltaurates, lignin sulfonates, naphthalene sulfonate formaldehyde condensates, polycarboxylates, and polyoxyethylene/polyoxypropylene block copolymers. Solid diluents include, for example, clays such as bentonite, montmorillonite, attapulgite and kaolin, starch, sugar, silica, talc, diatomaceous earth, urea, calcium carbonate, sodium carbonate and bicarbonate, and sodium sulfate. Liquid diluents include, for example, water, *N,N*-dimethylformamide, dimethyl sulfoxide, *N*-alkylpyrrolidone, ethylene glycol, polypropylene glycol, paraffins, alkylbenzenes, alkylnaphthalenes, oils of olive, castor, linseed, tung, sesame, corn, peanut,

cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone, and alcohols such as methanol, cyclohexanol, decanol and tetrahydrofurfuryl alcohol.

Solutions, including emulsifiable concentrates, can be prepared by simply mixing the ingredients. Dusts and powders can be prepared by blending and, usually, grinding as in a hammer mill or fluid-energy mill. Suspensions are usually prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be prepared by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147-48, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, 1963, pages 8-57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can be prepared as taught in U.S. 4,144,050, U.S. 3,920,442 and DE 3,246,493. Tablets can be prepared as taught in U.S. 5,180,587, U.S. 5,232,701 and U.S. 5,208,030. Films can be prepared as taught in GB 2,095,558 and U.S. 3,299,566.

For further information regarding the art of Formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10-41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, 1961, pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are prepared in conventional ways. Compound numbers refer to compounds in Index Table A.

Example A

Wettable Powder

Compound 7	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 7	10.0%
attapulgite granules (low volatile matter, 0.71/0.30 mm; U.S.S. No. 25–50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 7	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

Compound 7	20.0%
blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, stem or root feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropods" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all growth stages of all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, juveniles and adults of the Phylum Nematoda. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Siphonaptera, Blattaria, Thysanura and Psocoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. Specifically, the compounds are active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrosteles fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera frugiperda*), black bean aphid (*Aphis fabae*), green peach aphid (*Myzus persica*), cotton aphid (*Aphis gossypii*), Russian wheat aphid (*Diuraphis noxia*), English grain aphid (*Sitobion avenae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug

(*Scotinophara lurida*), rice stink bug (*Oebalus pugnax*), rice bug (*Leptocorisa chinensis*), slender rice bug (*Cletus puntiger*), and southern green stink bug (*Nezara viridula*). The compounds are active on mites, demonstrating ovicidal, larvicidal and chemosterilant activity against such families as Tetranychidae including *Tetranychus urticae, Tetranychus cinnabarinus, Tetranychus mcdanieli, Tetranychus pacificus, Tetranychus turkestani, Byrobia rubrioculus, Panonychus ulmi, Panonychus citri, Eotetranychus carpini borealis, Eotetranychus, hicoriae, Eotetranychus sexmaculatus, Eotetranychus yumensis, Eotetranychus banksi* and *Oligonychus pratensis*; Tenuipalpidae including *Brevipalpus lewisi, Brevipalpus phoenicis, Brevipalpus californicus* and *Brevipalpus obovatus*; Eriophyidae including *Phyllocoptruta oleivora, Eriophyes sheldoni, Aculus cornutus, Epitrimerus pyri* and *Eriophyes mangiferae.* See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, growth regulators, chemosterilants, semiochemicals, repellents, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of such agricultural protectants with which compounds of this invention can be formulated are: insecticides such as abamectin, acephate, azinphos-methyl, bifenthrin, buprofezin, carbofuran, chlorfenapyr, chlorpyrifos, chlorpyrifos-methyl, cyfluthrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, deltamethrin, diafenthiuron, diazinon, diflubenzuron, dimethoate, esfenvalerate, fenoxycarb, fenpropathrin, fenvalerate, fipronil, flucythrinate, tau-fluvalinate, fonophos, imidacloprid, isofenphos, malathion, metaldehyde, methamidophos, methidathion, methomyl, methoprene, methoxychlor, methyl 7-chloro-2,5-dihydro-2-[[*N*-(methoxycarbonyl)-*N*-[4-(trifluoromethoxy)phenyl]amino]carbonyl]indeno[1,2-*e*][1,3,4]oxadiazine-4a(3*H*)-carboxylate (DPX-JW062), monocrotophos, oxamyl, parathion, parathion-methyl, permethrin, phorate, phosalone, phosmet, phosphamidon, pirimicarb, profenofos, rotenone, sulprofos, tebufenozide, tefluthrin, terbufos, tetrachlorvinphos, thiodicarb, tralomethrin, trichlorfon and triflumuron; fungicides such as acibenzolar, azoxystrobin, binomial, blasticidin-S, Bordeaux mixture (Triassic copper sulfate), bromuconazole, capropamid (KTU 3616), captafol, captan, carbendazim, chloroneb, chlorothalonil, copper oxychloride, copper salts, cymoxanil, cyproconazole, cyprodinil (CGA 219417),(*S*)-3,5-dichloro-*N*-(3-chloro-1-ethyl-1-methyl- 2-oxopropyl)-4-methylbenzamide (RH 7281), diclocymet (S-2900), diclomezine, dicloran, difenoconazole,(*S*)-3,5-dihydro-5-methyl-2-(methylthio)-5-phenyl- 3-(phenylamino)-4*H*-imidazol-4-one (RP 407213), dimethomorph, diniconazole, diniconazole-M, dodine, edifenphos, epoxiconazole (BAS 480F), famoxadone, fenarimol, fenbuconazole, fencaramid (SZX0722), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, fluazinam, fludioxonil, flumetover (RPA 403397),

fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fosetyl-aluminum, furalaxyl, furametapyr (S-82658), hexaconazole, ipconazole, iprobenfos, iprodione, isoprothiolane, kasugamycin, kresoxim-methyl, mancozeb, maneb, mefenoxam, mepronil, metalaxyl, metconazole, metominostrobin/fenominostrobin (SSF-126), myclobutanil, neo-asozin (ferric methanearsonate), oxadixyl, penconazole, pencycuron, probenazole, prochloraz, propamocarb, propiconazole, pyrifenox, pyrimethanil, pyroquilon, quinoxyfen, spiroxamine, sulfur, tebuconazole, tetraconazole, thiabendazole, thifluzamide, thiophanate-methyl, thiram, triadimefon, triadimenol, tricyclazole, triticonazole, validamycin and vinclozolin; nematocides such as aldoxycarb and fenamiphos; bactericides such as streptomycin; acaricides such as amitraz, chinomethionat, chlorobenzilate, cyhexatin, dicofol, dienochlor, etoxazole, fenazaquin, fenbutatin oxide, fenpropathrin, fenpyroximate, hexythiazox, propargite, pyridaben and tebufenpyrad; and biological agents such as *Bacillus thuringiensis*, *Bacillus thuringiensis* delta endotoxin, baculovirus, and entomopathogenic bacteria, virus and fungi.

In certain instances, combinations with other arthropodicides having a similar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

Arthropod pests are controlled and protection of agronomic, horticultural and specialty crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. Thus, the present invention further comprises a method for the control of foliar and soil inhabiting arthropods and nematode pests and protection of agronomic and/or nonagronomic crops, comprising applying one or more of the compounds of the invention, or compositions containing at least one such compound, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, seed coats, microencapsulations, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, dusts and many others. The compounds can be incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

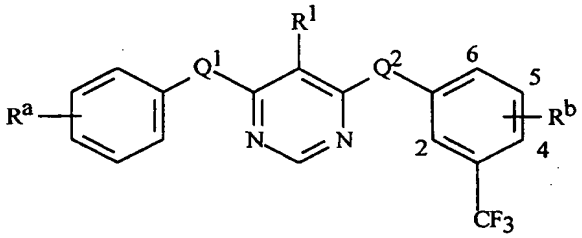
The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil

concentrates, spreader stickers, adjuvants, other solvents, and synergists such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

The following Test A demonstrates the control efficacy of compounds of this invention on specific pests. "Control efficacy" represents inhibition of arthropod development (including mortality) that causes significantly reduced feeding. The pest control protection afforded by the compounds is not limited, however, to this species. See Index Tables A-B for compound descriptions. The abbreviation "Ex." stands for "Example" and is followed by a number indicating in which example the compound is prepared.

INDEX TABLE A



Compound	Q^1	Q^2	R^a	R^b	R^1	Physical Property (m.p. °C)*
1	CH_2	O	H	H	H	a
2 (Ex. 2)	CO	O	H	H	H	b
3	CO	O	F	H	H	c
4	CO	O	F	F	H	d
5	CH_2	O	H	F	H	e
6	CH_2	O	F	F	H	f
7 (Ex. 1)	CH_2	O	F	H	H	g
8	CH_2	O	F	Cl	H	h
9	CH_2	O	H	Cl	H	i
10	CH_2	O	F	NO_2	H	j
11	CO	NH	F	F	H	150-153
12 (Ex. 3)	CH_2	NH	H	F	H	102-104

13	CF_2	O	3-CF_3, 4-Cl	4-F	H	k
14	CH_2	O	3-CF_3, 4-F	5-F	H	l
15	CO	O	3-CF_3, 4-Cl	4-F	H	m
16	CH_2	O	3-CF_3, 4-F	2-F	H	n
17	CH_2	O	3-CF_3, 4-F	6-F	H	o
18	CF_2	O	3-CF_3, 4-F	4-F	H	p
19	CO	O	3-CF_3, 4-F	4-Cl	H	q
20	CO	O	3-CF_3, 4-F	5-F	H	r
21(Ex. 5)	CH_2	O	3-CF_3, 4-F	4-F	NH_2	s
22	CH_2	O	3-CF_3	4-F	NH_2	t
23	CH_2O	O	3-CF_3, 4-F	4-F	H	u
24	CH_2O	O	4-CF_3	4-F	H	58-60
25	CH_2O	O	2,3-diF	4-F	H	v
26	CH_2O	O	3-CF_3, 4-F	H	H	71-73
27 (Ex. 4)	CH_2O	O	3-CF_3	4-F	H	w
28	CH_2O	O	2-CF_3	4-F	H	x
29	CH_2O	O	3-CF_3, 4-F	4-Cl	H	y
30	CH_2O	O	3,4-diF	4-F	H	z
31	CH_2O	O	3-CF_3, 2-F	4-F	H	aa
32	CH_2O	O	3-CF_3, 4-F	4-F	NH_2	bb
33	CH_2O	O	3,4-diCl	4-F	H	cc
34	$CH(CF_3)O$	O	H	4-F	H	dd
35	CH_2O	O	4-CF_3, 2-F	4-F	H	ee
36	$CH(CH_3)O$	O	3,4-diCl	4-F	H	ff
37	CH_2O	O	4-Cl	4-F	H	gg
38	CH_2O	O	3-NO_2, 4-Cl	4-F	H	hh
39	S	O	3-F	4-F	H	ii
40	S	O	2-F	4-F	H	jj
41	S	O	4-F	4-F	H	kk
42	S	O	3-CF_3	4-F	H	72-73
43	S	O	2-Cl, 4-F	4-F	H	53-60
44	CH_2S	O	4-OMe, 3-Cl	4-F	H	91-94
45	CH_2S	O	4-OMe	4-F	H	66-69
46	CH_2S	O	2-Cl	4-F	H	ll
47 (Ex. 6)	CH_2S	O	4-Cl	4-F	H	66-69

*See Index Table B for ^{1}H NMR data.

INDEX TABLE B

^{1}H NMR in $CDCl_3$ (δ)

a) 4.16 (s,2H), 6.74 (s,1H), 7.35 m,1H), 7.41 (s,1H), 7.45-7.80 (m,6H), 8.71 (s,1H).

b) 7.38-7.45 (m,1H), 7.49 (s,1H), 7.61 (d,3H), 7.62-7.72 (m,1H), 7.90 (d,1H), 8.38 (d,1H), 8.44 (s,1H), 8.92 (s,1H).

c) 7.23-7.42 (m,3H), 7.45 (m,1H), 7.63 (s,1H), 8.42-8.60 (m,2H), 8.86 (s,1H).

d) 7.27-7.54 (m,3H), 7.60-7.73 (m,2H), 7.85-7.95 (m,1H), 8.31-8.39 (m,1H), 8.46 (s,1H), 8.90 (s,1H).

e) 4.16 (s,2H), 6.74 (s,1H), 7.2-7.42 (m,3H), 7.44-7.60 (m,4H), 8.69 (s,1H).

f) 4.13 (s,2H), 6.76 (s,1H), 7.16-7.38 (m,3H), 7.38-7.41 (m,1H), 7.45-7.57 (m,2H), 8.68 (s,1H).

g) 4.11 (s,2H), 6.75 (s,1H), 7.18 (t,1H), 7.28-7.38 (m,1H), 7.42 (s,1H), 7.43-7.60 (m,2H), 8.70 (s,1H).

h) 4.16 (s,1H), 6.77 (s,1H), 7.20 (m,1H), 7.28 (m,1H), 7.45-7.60 (m,4H), 8.69 (s,1H).

i) 4.16 (s,2H), 7.26-7.32 (m,1H), 7.43-7.60 (m,6H), 8.70 (s,1H).

j) 4.15 (s,2H), 6.83 (s,1H), 7.20 (m,1H), 7.44-7.58 (m,3H0, 7.63 (s,1H), 8.02 (d,1H), 8.77 (s,1H).

k) 7.28 (t, 1H), 7.3-7.45 (m, 3H), 7.4 (d, 1H), 7.8 (d, 1H).

l) 4.13 (s, 2H), 6.78 (s, 1H), 7.15 (m, 2H), 7.25 (m, 2H0, 8.7 (m, 1H).

m) 7.31 (t, 1H), 7.35-7.5 (m, 3H), 7.58-7.76 (m, 2H), 8.35 (d, 1H), 8.58 (s, 1H), 8.9 (s, 1H).

n) 4.13 (s, 2H), 6.83 (s, 1H), 7.19 (t, 1H), 7.29 (t, 1H), 7.38-7.6 (m, 4H), 8.68 (s, 1H).

o) 4.13 (s, 1H), 6.83 (s, 1H), 7.2 (t, 1H), 7.43-7.6 (m, 4H), 8.68 (s, 1H).

p) 7.3-7.45 (m, 5H), 7.83-7.97 (m, 2H), 8.76 (s, 1H).

q) 7.3-7.41 (m, 2H), 7.49-7.65 (m, 3H), 8.43-8.52 (m, 1H), 8.78 d, 1H), 8.94 (s, 1H).

r) 7.2-7.4 (m, 4H), 7.6 (s, 1H), 8.5 (m, 1H), 8.6 (m, 1H), 8.9 (s, 1H).

s) 3.83 (s, 2H), 4.2 (s, 2H), 7.17 (t, 1H), 7.2-7.58 (m, 5H), 8.19 (s, 1H).

t) 3.81 (s, 2H0, 4.16 (s, 2H), 7.26 (t, 1H), 7.32-7.58 (m, 6H), 8.2 (s, 1H).

u) 5.46 (s, 2H), 6.31 (s, 1H), 7.43-7.18 (m, 4H), 7.75-7.60 (m, 2H), 8.43 (s, 1H).

v) 5.53 (s, 2H), 6.30 (s, 1H), 7.43-7.05 (m, 6H), 8.44 (s, 1H).

w) 5.51 (s, 2H), 6.32 (s, 1H), 7.65-7.20 (m, 6H), 7.71 (s, 1H), 8.44 (s, 1H).

x) 8.61 (s, 1H), 7.75-7.45 (m's, 7H), 6.86 (s, 1H), 5.64 (s, 2H).

y) 8.43 (s, 1H), 7.75-7.15 (m's, 6H), 6.32 (s, 1H), 5.46 (s, 2H).

z) 8.42 (s, 1H), 7.45-7.15 (m's, 6H), 6.29 (s, 1H), 5.40 (s, 2H).

aa) 8.45 (s, 1H), 7.75-7.20 (m's, 6H), 6.31 (s, 1H), 5.57 (s, 2H).

bb) 7.90 (s, 1H), 7.75-7.15 (m's, 6H), 5.50 (s, 2H), 3.82 (broad s, 2H) .

cc) 8.43 (s, 1H), 7.57-7.0 (m's, 6H), 6.29 (s, 1H), 5.40 (s, 2H.

dd) 8.40 (s, 1H), 7.60-7.20 (m's, 8H), 6.65 (q, 1H), 6.45 (s, 1H).

ee) 8.44 (s, 1H), 7.65-7.20 (m's, 6H), 6.33 (s, 1H), 5.57 (s, 2H).

ff) 8.35 (s, 1H), 7.55-7.20 (m's, 6H), 6.26 (s, 1H), 6.20 (q, 1H), 1.63 (d, 3H).

gg) 8.45 (s, 1H), 7.45-6.95 (m's, 7H), 6.26 (s, 1H), 5.41 (s, 2H).

hh) 8.59 (s, 1H), 7.97 (s, 1H), 7.58 (s, 2H), 7.27 (m, 3H), 6.87 (s, 1H), 5.48 (s, 2H).

ii) 8.51 (s, 1H), 7.4-7.1 (m, 7H), 6.39 (s, 1H).

jj) 8.50 (s, 1H), 7.7-7.1 (m, 7H), 6.41 (s, 1H)

kk) 8.50 (s, 1H), 7.6-7.0 (m, 7H), 6.33 (s, 1H).

ll) 8.58 (s, 1H), 7.5-7.2 (m, 7H), 6.76 (s, 1H), 4.6 (s, 2H)

^{1}H NMR data are in ppm downfield from tetramethylsilane. Couplings are designated by (s)-singlet, (d)-doublet, (t)-triplet, (q)-quartet, (m)-multiplet, (dd)-doublet of doublets, (dt)-doublet of triplets, (br s)-broad singlet.

BIOLOGICAL EXAMPLES OF THE INVENTION

TEST A

Two-Spotted Spider Mite

Pieces of kidney bean leaves, each approximately 6.5 cm^2 (1 square inch) in area, that had been infested on the undersides with 25 to 30 adult mites (*Tetranychus urticae*), were sprayed with their undersides facing up on a hydraulic sprayer with a solution of the test compound in 75:25 acetone-distilled water solvent. Spraying was accomplished by passing the leaves, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.138 kilograms of active ingredient per hectare (about 0.13 pounds per acre) at 207 kPa (30 p.s.i.). The leaf squares were then placed underside-up on a square of wet cotton in a petri dish and the perimeter of the leaf square was tamped down onto the cotton with forceps so that the mites could not escape onto the untreated leaf surface. The test units were held at 27°C and 50% relative humidity for 48 hours, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 35, 37, 39, 40, 41, 42 and 43.

TEST B

Fall Armyworm

Test units, each consisting of a H.I.S. (high impact styrene) tray with 16 cells were prepared. Wet filter paper and approximately 8 cm^2 of lima bean leaf was placed into twelve of the cells. A 0.5-cm layer of wheat germ diet was placed into the four remaining cells. Fifteen to twenty third-instar larvae of fall armyworm (*Spodoptera frugiperda*) were placed into a 230-mL (8-ounce) plastic cup. Solutions of each of the test compounds in 75:25 acetone-distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup on a conveyer belt directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.138 kilograms of active ingredient per hectare (about 0.13 pounds per acre) at 207 kPa (30 p.s.i.). The insects were transferred from the 230-mL cup to the H.I.S. tray (one insect per cell). The trays were covered and held at 27°C and 50% relative humidity for 48 hours, after which time readings were taken on the twelve cells with lima bean leaves. The four remaining cells were read at 6-8 days for

delayed toxicity. Of the compounds tested, the following gave control efficacy levels of 80% or greater: 41.

TEST C

Corn Planthopper Test

Test Unit: The test unit consisted of a plastic cup containing 126 +/- 4 grams of sterilized, non-fertilized sassafras (sandy loam) soil. One pre-germinated Pioneer variety 3394 corn seed is placed in a 1 inch depression in the soil and covered. The test unit was watered with 15mL of distilled water and placed in a closed plexiglas box inside a greenhouse operating at 24 degrees centigrade and 36% relative humidity for 4 days at which time it is ready for test. A snug-fitting test unit lid with a small opening at the top was placed on all test units prior to test.

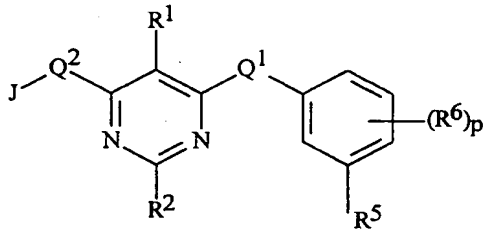
Compound Application: Test compounds were formulated at 250 ppm in 20% acetone: 80% water containing 500 ppm Ortho X-77 surfactant. Compounds were applied through the opening in the test unit lid with an atomizer sprayer fitted with a Model 17690-1/8JJAU nozzle and a spray set-up consisting of a J2850 Fluid Cap and J70 Air Cap (Spray Sytems, Inc.). The sprayer was operated at 12-13psi. For each compound, 2 test units were sprayed with a total of 2 mL each of test solution. After spraying, test units were placed in a ventilated enclosure for 10-15 minutes to dry.

Insect Infesting/Evaluation: After drying, a thin layer of white quartz sand was poured onto the soil of each test unit to aid in the evaluation of live and dead insects at the conclusion of the test. Each unit was infested with a minimum of 15 nymphs of the corn planthopper, Peregrinus maidis, which were approximately 21 days old. Infested test units were held in a growth chamber operating at 22 degrees centigrade and 50% relative humidity with a 16:8 light:dark photoperiod. Insect mortality was evaluated at 6 days post-infestation. Moribund insects were counted as dead. Of the compounds tested, the following gave mortality of 80% or greater: 42.

CLAIMS

What is claimed is:

1. A compound selected from Formula I, *N*-oxides and agriculturally suitable salts thereof,



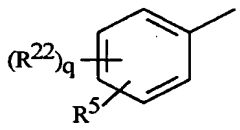
I

wherein

Q^1 is O, S, NR^{17}, $OCR^{18}R^{19}$, or $NR^{17}CR^{18}R^{19}$; wherein when Q^1 is $OCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$, then Q^1 is attached to the pyrimidine through the O or N atom respectively;

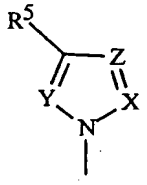
Q^2 is S, CR^3R^4, $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$; wherein when Q^2 is $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$ then Q^2 is attached to the pyrimidine through the O, S or N atom respectively;

J is



J^1

or



J^2

X, Y and Z are each independently N or CR^{22};

R^1 and R^2 are each independently H, C_1-C_4 alkyl, halogen, NR^7R^8, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkylthio or nitro;

R^3 and R^4 are each independently H, halogen, hydroxy, C_1-C_4 alkyl, C_1-C_4 alkoxy, C_1-C_4 haloalkyl or cyano; or R^3 and R^4 are taken together with the attached carbon to make a carbonyl;

each R^5 is independently H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11};

each R^6 and each R^{22} is independently H, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_1-C_4 alkoxy, NR^{17} or $S(O)_nR^9$;

R^7 and R^8 are each independently H, C_1-C_4 alkyl, C_3-C_6 alkenyl, C_3-C_6 alkynyl, COR^{10}, CO_2R^{11}, CHO, SO_2R^{12} or OR^{13};

each R^9 is independently C_1-C_4 alkyl or C_1-C_4 haloalkyl;

each R^{10} is independently C_1-C_6 alkyl, phenyl optionally substituted by R^6, C_1-C_6 haloalkyl, CO_2R^{14}, C_1-C_6 alkoxyalkyl, C_2-C_4 alkenyl, C_2-C_6 alkynyl, C_2-C_6 cyanoalkyl or $NR^{15}R^{16}$;

R^{11} and R^{12} are each independently C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl or C_2-C_6 alkynyl;

R^{13} and R^{17} are each independently C_1-C_4 alkyl, H, COR^{10} or CO_2R^{11};

each R^{14} is independently C_1-C_4 alkyl;

each R^{15} is independently H, C_1-C_4 alkyl, C_1-C_4 alkoxy or phenyl optionally substituted by R^6;

R^{16} and R^{19} are each independently H or C_1-C_4 alkyl;

each R^{18} is independently H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, or cyano;

n is 0-2;

p is 0-4; and

q is 0-4;

provided that when Q^2 is $NR^{17}CR^{18}R^{19}$, then J is J^2.

2. A compound of Claim 1 wherein

J is J^1;

R^1 and R^2 are H;

R^5 is C_1-C_2 haloalkyl;

each R^6 and each R^{22} is halogen; and

R^3 and R^4 are either each H or taken together with the attached carbon as a carbonyl.

3. A compound of Claim 1 wherein

J is J^2;

R^1 and R^2 are H;

R^5 is C_1 to C_2 haloalkyl;

each R^6 and each R^{22} is halogen;

R^3 and R^4 are each H; and

Y is N, X is CH and Z is CR^{22}.

4. A compound of Claim 2 selected from the group:

4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]pyrimidine;

4-[4-chloro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]pyrimidine;

[6-[4-fluoro-3-(trifluoromethyl)phenoxy]-4-pyrimidinyl][4-fluoro-3-(trifluoromethyl)phenyl]methanone;

4-[4-fluoro-3-(trifluoromethyl)phenyl]-6-[3-(trifluoromethyl)-phenyl]methoxypyrimidine;
4-[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[[4-fluoro-3-(trifluoromethyl)phenyl]methyl]-5-pyrimidinamine;
4-[(3,4-difluorophenyl)methoxy]-6-[4-fluoro-3-(trifluoromethyl)phenoxy]pyrimidine and
4-[4-fluoro-3-(trifluoromethyl)phenoxy]- 6-[(4-fluorophenyl)thio]pyrimidine.

5. An arthropodicidal composition comprising an arthropodicidally effective amount of a compound of Claim 1 and at least one of a surfactant, a solid diluent or a liquid diluent.

6. A method for controlling arthropods comprising contacting the arthropods or their environment with an arthropodicidally effective amount of a compound of Claim 1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 August 2000 (24.08.2000)

PCT

(10) International Publication Number
WO 00/49001 A3

(51) International Patent Classification[7]: C07D 239/34, 239/38, 239/42, 239/46, 239/52, 239/56, 403/06

(21) International Application Number: PCT/US00/03180

(22) International Filing Date: 8 February 2000 (08.02.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/120,130 16 February 1999 (16.02.1999) US
60/139,302 15 June 1999 (15.06.1999) US

(71) Applicant *(for all designated States except US)*: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: STEVENSON, Thomas, Martin [US/US]; 103 Iroquois Court, Newark, DE 19702 (US).

(74) Agent: BIRCH, Linda, D.; E.I. Du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19808 (US).

(81) Designated States *(national)*: AE, AL, AU, BA, BB, BG, BR, CA, CN, CR, CU, CZ, DM, EE, GD, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ZA.

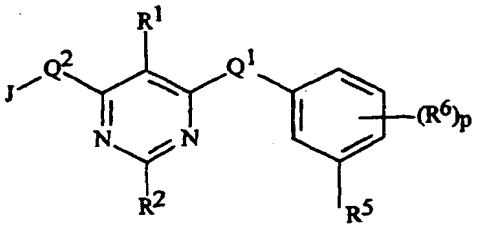
(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

(88) Date of publication of the international search report:
21 December 2000

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PHENOXY-, PHENYLTHIO-, PHENYLAMINO-, BENZYLOXY-, BENZYLTHIO- OR BENZYLAMINOPYRIMIDINE INSECTIDICES AND ACARICIDES



(I)

(57) Abstract: Compounds of Formula (I), and their *N*-oxides and agriculturally suitable salts, are disclosed which are useful as arthropodicides wherein Q^1 is O, S, NR^{17}, $OCR^{18}R^{19}$, or $NR^{17}CR^{18}R^{19}$; wherein when Q^1 is $OCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$, then Q^1 is attached to the pyrimidine through the O or N atom respectively; Q^2 is S, CR^3R^4, $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$; wherein when Q^2 is $OCR^{18}R^{19}$, $SCR^{18}R^{19}$ or $NR^{17}CR^{18}R^{19}$ then Q^2 is attached to the pyrimidine through the O, S or N atom respectively; R^1 and R^2 are each independently H, C_1-C_4 alkyl, halogen, NR^7R^8, C_1-C_4 alkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkylthio or nitro; each R^5 is independently H, halogen, C_1-C_4 alkyl, C_1-C_4 haloalkoxy, C_1-C_4 haloalkyl, C_1-C_4 alkoxy, SF_5, $S(O)_nR^9$, cyano or CO_2R^{11}; each R^6 and each R^{22} is independently H, halogen, cyano, C_1-C_4 alkyl, C_1-C_4 haloalkyl, C_1-C_4 haloalkoxy, C_1-C_4 alkoxy, NR^{17} or $S(O)_nR^9$; p is 0-4; and J, R^3, R^4R^7, R^8, R^9, R^{11}, R^{17}, R^{18}, R^{19} and n are as defined in the disclosure. Also disclosed are compositions containing the compounds of Formula (I) and a method for controlling arthropods which involves contacting the arthropods or their environment with an effective amount of a compound of Formula (I).

WO 00/49001 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03180

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D239/34 C07D239/38 C07D239/42 C07D239/46 C07D239/52
C07D239/56 C07D403/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 707 995 A (DAVIS ROYSTON ET AL) 13 January 1998 (1998-01-13) cited in the application see compounds 7,8,9 column 1, line 18 - line 60 ---	1-6
P,X	EP 0 972 770 A (AMERICAN CYANAMID COMPANY, USA) 19 January 2000 (2000-01-19) claims 1-10; examples 1-16,19,30-41 ---	1-6
A	WO 98 54154 A (NAKAMURA TAKEHIKO ;TAKAHASHI HIDEMITSU (JP); IWASA TAKAO (JP); HAM) 3 December 1998 (1998-12-03) the whole document ---	1-6
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 June 2000	02 OCT 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schmid, J-C

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03180

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 12184 A (ISHIMITSU KEIICHI ;NAKAMURA TAKEHIKO (JP); TAKAHASHI HIDEMITSU (JP) 26 March 1998 (1998-03-26) the whole document	1-6
P,A	JP 11 269154 A (NIPPON SODA CO LTD) 5 October 1999 (1999-10-05) cited in the application the whole document	1-6
X	WO 97 14684 A (JANSSEN PHARMACEUTICA N.V., BELG.;NEUROCRINE BIOSCIENCES INC.; WEBB, T) 24 April 1997 (1997-04-24) see table 5	1,2
P,X	EP 0 945 442 A (JANSSEN PHARMACEUTICA N.V., BELG.) 29 September 1999 (1999-09-29) see table 4 claim 1	1,2
P,X	WO 99 50250 A (JANSSEN PHARMACEUTICA N.V., BELG.;ET AL.) 7 October 1999 (1999-10-07) see tables 3-5	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/03180

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 6 (all partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

1. Claims: 1-6 (all partially)

those pyrimidine derivatives of formula (I) wherein Q2 is CR3R4.
This group can be represented by the claimed compound 6[4-fluoro-3-(trifluoromethyl)phenoxy]-4-pyrimidinyl] [4-fluoro-3-(trifluoromethyl)phenyl]methanone -see claim 4.

2. Claims: claim 1-6 (al part)

those pyrimidine derivatives of formula (I) wherein Q2 is OCR18R19, SCR18R19 or NR17CR18R19 and those Q2 is S and Q1 is OCR18R19 or NR17CR18R19.
This group can be represented by the claimed compound 4[3,4-difluorophenyl)methoxy]-6-[(4-fluoro-3-trifluoromethyl-phenoxy]pyrimidine.

3. Claims: 1-6 (all partially)

those pyrimidine derivatives of formula (I) wherein Q2 is S and Q1 is O or NR17.
This group can be represented by the claimed compound 4[4-fluoro-3-(trifluoromethyl)phenoxy]-6-[(4-fluorophenyl) thio]pyrimidine.

4. Claims: 1,3-6 (all partially)

those pyrimidine derivatives of formula (I) wherein Q1=Q2=S.
There are no working examples which can represent this group.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/03180

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5707995 A	13-01-1998	AU 671845 B	12-09-1996
		AU 4570093 A	14-02-1994
		CA 2140346 A	03-02-1994
		CN 1087085 A	25-05-1994
		CZ 9500030 A	13-09-1995
		EG 20267 A	31-05-1998
		WO 9402470 A	03-02-1994
		EP 0650482 A	03-05-1995
		HU 70086 A	28-09-1995
		IL 106324 A	24-09-1998
		JP 7508999 T	05-10-1995
		MD 950235 A	31-10-1997
		PL 307131 A	02-05-1995
		PL 173066 B	30-01-1998
		PL 173717 B	30-04-1998
		PL 173091 B	30-01-1998
		PL 173056 B	30-01-1998
		PL 173467 B	31-03-1998
		SG 49712 A	15-06-1998
		SK 3295 A	10-05-1995
		TR 26781 A	15-05-1995
		ZA 9305155 A	20-06-1994
EP 0972770 A	19-01-2000	JP 2000080084 A	21-03-2000
WO 9854154 A	03-12-1998	AU 7452998 A	30-12-1998
WO 9812184 A	26-03-1998	AU 4221797 A	14-04-1998
JP 11269154 A	05-10-1999	NONE	
WO 9714684 A	24-04-1997	AU 703096 B	18-03-1999
		AU 7292996 A	07-05-1997
		CA 2229710 A	24-04-1997
		EP 0863882 A	16-09-1998
		JP 11513678 T	24-11-1999
		NO 981623 A	09-06-1998
		NZ 320227 A	25-11-1998
EP 0945442 A	29-09-1999	AU 3599699 A	18-10-1999
		WO 9950250 A	07-10-1999
		EP 0945443 A	29-09-1999
WO 9950250 A	07-10-1999	AU 3599699 A	18-10-1999
		EP 0945443 A	29-09-1999
		EP 0945442 A	29-09-1999